

$$(m_d - m_b) = \frac{k_2}{k_\phi} (m_o - 1) + \frac{k_r}{k_\phi} (m_b - m_o) \quad (1)$$

$$(m_o - m_c) = \frac{k_2}{k_\phi} m_o + \frac{k_r}{k_\phi} (m_c - m_d) \quad (2)$$

$$(m_b - m_d) = \frac{k_2}{k_\phi} m_d + \frac{k_r}{k_\phi} (m_d - m_o) \quad (3)$$

$$(m_o - m_e) = \frac{k_2}{k_\phi} m_o + \frac{k_r}{k_\phi} (m_o - m_d) \quad (4)$$

The extent of error in calculating these values is illustrated by using them to recalculate $m_b - m_e$ from eq. 1-4. The observed and calculated mole fractions are in good agreement, and are listed in Table I (runs 1-3).

The same calculations were applied to the data obtained for the thermal decomposition of N-acetyl-N-nitroso-1,2,2-triphenylethylamine,² which has been postulated to go through the same intermediates. The results are given in Table I (run no. 4).

The results in Table I demonstrate the compatibility of the classical carbonium ion mechanism of Chart I with the data both for the deaminations^{1,2} and for the thermal decomposition of N-acetyl-N-nitroso-1,2,2-triphenylethylamine. They also provide quantitative information concerning the relationship between k_2 , k_ϕ , and k_r , which are shown to be of the same order of magnitude for the reactions studied. Equations 1-4 in addition permit us to calculate the extent of carbon¹⁴ rearrangement and the amount of inversion for all possible values of k_2/k_ϕ and k_r/k_ϕ .

Acknowledgment.—We wish to acknowledge helpful discussions with Drs. M. H. Lietzke, R. W. Stoughton, and William Busing.

(14) Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

OAK RIDGE NATIONAL LABORATORY¹⁴
OAK RIDGE, TENNESSEE

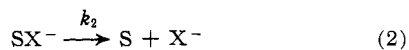
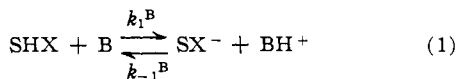
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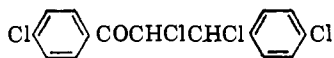
Kinetic Evidence for the Carbanion Mechanism of Dehydrohalogenation

Sir:

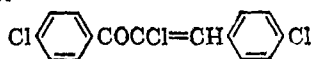
The two-step character of the E_1CB (carbanion) mechanism of certain base-catalyzed elimination reactions¹ should be disclosed not only by exchange^{1c,d} and stereochemical^{1e} evidence, but also by kinetics^{1f} characteristic of the consecutive reactions 1 and 2.



We wish to report that the dehydrochlorination of erythro-4,4'-dichlorochalcone dichloride (I), studied in



I² erythro (m.p. 143.5°;
max 262 mμ, ε 19,000)
II² threo (m.p. 97.5°;
max 263 mμ, ε 18,000)



III² trans (m.p. 62°;
max 310 mμ, ε 21,400)
IV² cis (m.p. 101°;
max 262 mμ, ε 23,500)

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 422-423; (b) J. F. Bunnett, *Angew Chem.*, **74**, 731 (1962); (c) L. C. Leitch and H. J. Bernstein, *Can. J. Res.*, **38B** 35 (1950); (d) P. S. Skell and C. R. Hauser, *J. Am. Chem. Soc.*, **67**, 1661 (1945); (e) S. J. Cristol, *ibid.*, **69**, 338 (1947); C. H. DuPuy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1315 (1962); (f) J. Hine, R. Weisboeck, and O. B. Ramsay, *ibid.*, **83**, 1222 (1961).

(2) These compounds gave the correct C and H analyses. III was first prepared by R. T. K., and I by C. O. Hugvins, unpublished results (with S. F. Clark), University of Mississippi.

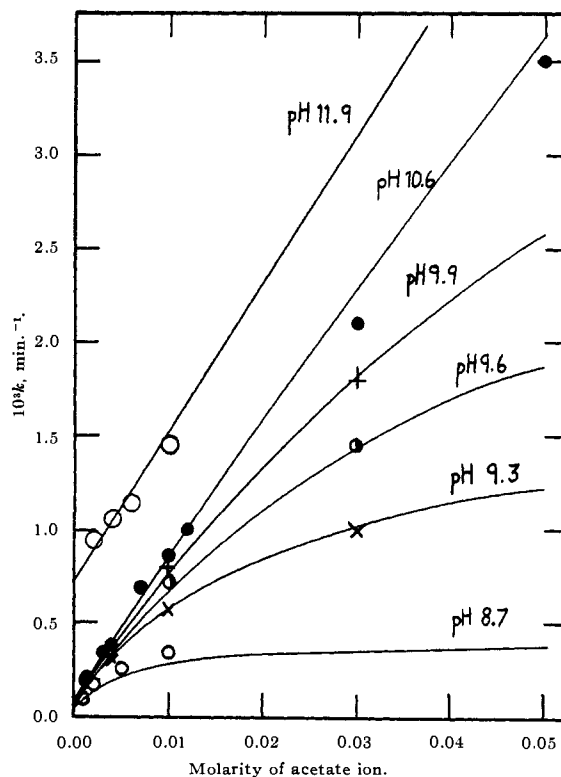


Fig. 1.—Family of curves (eq. 3) and experimental points showing pH dependence of the acetate-catalyzed elimination.

ethanolic acetate buffers, closely follows the rate equation³ (3) for the above mechanism in the range where the steady-state method is applicable.

$$k = \frac{k_2 K_{\text{SHX}} \Sigma k_1^{\text{B}} [\text{B}]}{k_2 K_{\text{SHX}} + [\text{H}^+] \Sigma k_1^{\text{B}} [\text{B}]} \quad (3)$$

The most striking demonstration of conformity with eq. 3 is shown in Fig. 1. The curves are calculated, with $k_1^{\text{EtOH}} = 5 \times 10^{-5} \text{ min.}^{-1}$, $k_1^{\text{EtO}^-} = 1.08 \times 10^4 \text{ l. mole}^{-1} \text{ min.}^{-1}$, $k_1^{\text{OAc}^-} = 7.9 \times 10^{-2} \text{ l. mole}^{-1} \text{ min.}^{-1}$, and $k_2 K_{\text{SHX}} = 9.1 \times 10^{-13}$. The ion product of ethanol is assumed to be 7.9×10^{-20} . The experimental points clearly show the required general base catalysis modified by the pH-dependent second term in the denominator of eq. 3. A high concentration either of buffer or of hydrogen ion will increase this term, so that k approaches $k_2 K_{\text{SHX}} / [\text{H}^+]$ and the rate itself approaches $k_2 [\text{SX}^-]$. This corresponds to a rate-controlling second step and under these conditions the curves of Fig. 1 level off as equilibrium is approached in the acid-base step (1).

Considering the uncertainties of pH measurement in absolute ethanol, the rates measured over a wider range of acidity are in satisfactory agreement with the calculated pH-rate profile (Fig. 2). The conditions used were: pH 5, hydrochloric or perchloric acid solutions (the dehydrohalogenation is practically halted at this acidity and is therefore self-decelerating when unbuffered⁴); pH 8-12, the acetate buffers of Fig. 1, extrapolated to zero concentration; pH 13, veronate buffers; pH 15-16, sodium ethoxide.

On the lower part of the pH-rate profile, step 2 is rate-controlling. As the pH increases past 8, a plateau appears as the second term in the denominator of eq. 3 becomes small and the ionization (1) rate-controlling with $\text{B} = \text{EtOH}$. Ethoxide ion begins to contribute appreciably as the base B around pH 10, causing a steady

(3) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 134-135. Equation 3 is an expression of the more obvious form, $k = k_2 \Sigma k_1^{\text{B}} [\text{B}] / (k_2 + \Sigma k_1^{\text{B}} [\text{B}])$, in terms of fewer constants.

(4) R. T. Kemp, Dissertation, University of Virginia, 1959.

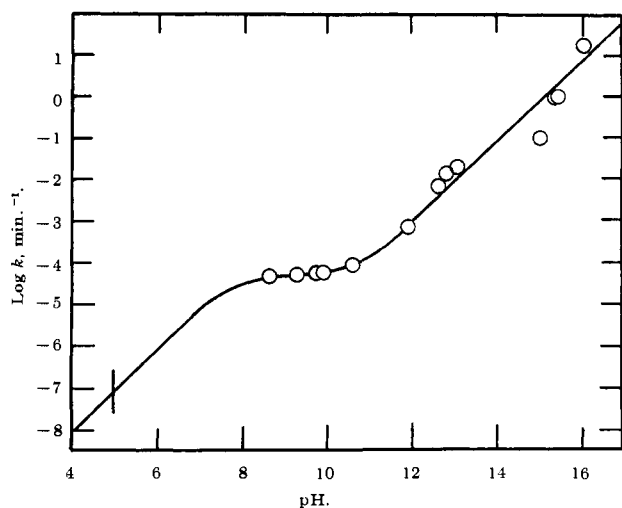
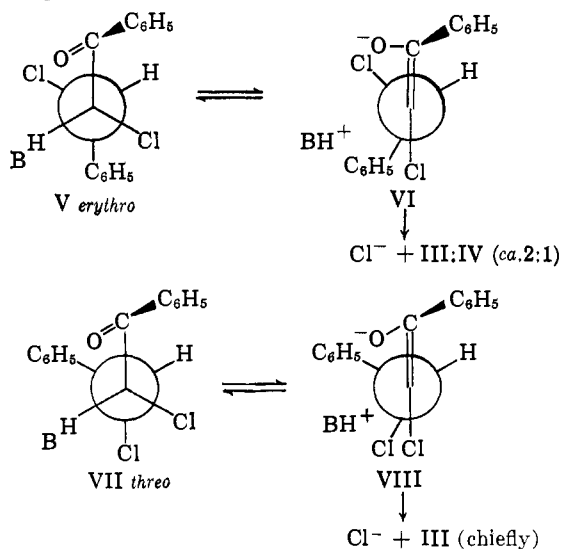


Fig. 2.—pH-rate profile (ethanol).

rise in rate at higher pH values. (Deuterium exchange of the acidic hydrogen atom of SHX would not be expected in this pH range since the reversal of the ionization step is much slower than the loss of chloride ion.) At pH 17, chloride production is complete in 2 sec., indicating that the expected leveling off of the rate, as step 1 becomes rapid and complete, has not commenced. This sets a lower limit of 70 min.^{-1} for k_2 .

The measurements were made by ultraviolet spectrophotometry at $282 \text{ m}\mu$, the isosbestic point of the products, the *trans* and *cis* chalcones III and IV. They are stable in the buffer solutions employed but are photochemically interconverted in diffuse light. Near pH 16, the rate of base consumption was observed by means of indicators.⁴

Preliminary experiments with the *threo* chalcone dichloride (II) point to kinetic behavior similar to the *erythro* form, but the k_1 values are higher. Since the course of the reaction is first order, there is at least no rapid conversion of the *threo* to the *erythro* form. The product contains a much higher proportion of *trans*-S. The relation of rate and products to the configuration of SHX is entirely in accord with a previously published study of the corresponding chalcone dibromides.⁵ The kinetic data here reported support the carbanion mechanism which was suggested for the *erythro* isomer but require modification of the concerted mechanism



(5) R. E. Lutz, D. F. Hinkley, and R. H. Jordan, *J. Am. Chem. Soc.*, **73**, 4647 (1951).

proposed.^{5,6} Possibly conformations related to those favored in the *erythro* and *threo* dichlorides, V and VII, persist in the very short-lived anions having the same, more stable enolate double bond configuration, VI and VIII. Group interferences coupled with solvent effects and ion pairing might contribute sufficiently to the energy barrier to rotation on the 2,3-dicarbon axis to direct return of the proton stereospecifically in the direction from which it had been abstracted. Subsequent irreversible separation of chloride ion from VI and VIII with attendant conformational adjustments could then bring about relatively nonstereospecific development of the α,β double bond in the end products III and IV. Thus the actually observed formation of different mixtures in the two cases of *trans* and *cis* products, with *trans* predominant, is understandable.

Acknowledgment.—We are grateful for the support of the National Science Foundation, Grant G-13292 (T. I. C.) and the U.S. Army Research Office (R. E. L.).

(6) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 492.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VIRGINIA

THOMAS I. CROWELL
ARTHUR A. WALL
ROBERT T. KEMP
ROBERT E. LUTZ

RECEIVED MAY 1, 1963

Trialkyl Phosphites: Novel Ring-Opening Reactions with Dimethylketene Dimers¹

Sir:

There have been numerous recent studies of reactions of trialkyl phosphites with carbonyl compounds, *e.g.*: α -diketones^{2a}; quinones^{2b,c}; α,β -unsaturated aldehydes, acids, and esters^{2d-f}; alkyl and aryl aldehydes^{2d}; diaryl ketones^{2g}; β -propiolactone^{2h}; and phthalic anhydride.²ⁱ Frequently, the product of reaction is an adduct. An example, the combination of diphenylketene with triethyl phosphite in 2:1 mole ratio, was described recently.³ Subsequent pyrolysis was reported to give triethyl phosphate, diphenylacetylene, and diphenylketene dimer.

We find that trialkyl phosphites also give adducts (1:1) with the dimers of dimethylketene, I and VIII. These adducts are evidently of a different type than that isolated from reaction of triethyl phosphite with diphenylketene monomer, as structures III and IX could not be expected to give analogous pyrolysis products.³ In addition, these reactions are of interest in that: (1) distinctly different adducts result from reaction with the two dimer forms in contrast to the single product normally formed from ring opening of either the dione or lactone-form dimer under attack by nucleophiles⁴ and (2) ring opening is accompanied by an apparent alkoxy group migration in preference to the alkyl group displacement or migration which is common in the various phosphonate-forming Arbuzov-type reactions of tri-

(1) Presented in part at the Southwest Regional Meeting of the American Chemical Society, Dallas, Texas, December, 1962.

(2) For references, see (a) F. Ramirez, N. Ramanathan, and N. B. Desai, *J. Am. Chem. Soc.*, **84**, 1317 (1962); (b) F. Ramirez, E. H. Chen, and S. Dershowitz, *ibid.*, **81**, 4338 (1959); (c) V. A. Kukhtin, N. S. Garif'yanov, and K. M. Orekhova, *Zh. Obshch. Khim.*, **31**, 1157 (1961); (d) V. A. Ginsberg and A. Ya. Yakubovich, *ibid.*, **30**, 3979, 3987 (1960); (e) G. Kamai and V. A. Kukhtin, *Dokl. Akad. Nauk SSSR*, **112**, 868 (1957); (f) G. Kamai and V. A. Kukhtin, *Zh. Obshch. Khim.*, **31**, 1735 (1961); (g) A. C. Posikus and J. E. Herweh, Abstracts of Papers of the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 17-O; (h) R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4453 (1956); (i) F. Ramirez, H. Yamanaka, and O. H. Basedow, *ibid.*, **83**, 173 (1961).

(3) T. Mukaiyama, H. Namku, and M. Okamoto, *J. Org. Chem.*, **27**, 3651 (1962).

(4) *E.g.*, by amines and alkoxide ions, R. H. Hasek, E. U. Elam, and J. C. Martin, *ibid.*, **26**, 4340 (1961).