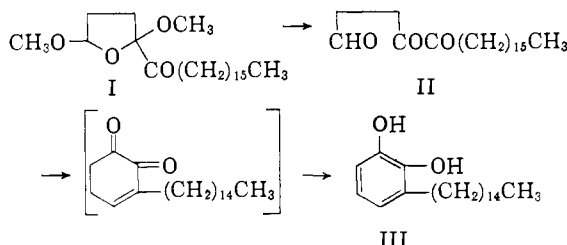


lac, cashew, mango and ginkgo trees.²⁻⁴ Cross-sensitivity between hydrourushiol and the extracts of other members of the Anacardiaceae^{8,5} has been demonstrated and hydrourushiol exhibits some advantages over the natural extracts in reducing immunologic sensitivity to *Rhus toxicodendron* dermatitis.⁶

We have been impressed by the ease with which certain furan derivatives are hydrolytically rearranged to form catechol. For example, Vargha and co-workers⁷ reported the formation of catechol from the cleavage product of *p*-toluenesulfonyl 2-acetofuranoxime and Clauson-Kaas and co-workers⁸ described the hydrolysis and spontaneous recyclization of 2-acetyl-2,5-dimethoxytetrahydrofuran dimethylketal to catechol. It appeared of interest, therefore, to synthesize some furanoid precursors of the catechol toxins which would hydrolyze *in vivo* to provide a low and lasting concentration of the allergen. This Communication describes the synthesis of 2-heptadecanoyl-2,5-dimethoxytetrahydrofuran (I) and its hydrolytic rearrangement to hydrourushiol (III) *in vitro*.



Methyl 2,5-dimethoxytetrahydrofuroate⁹ upon treatment with hexadecylmagnesium bromide gave 29% of 2-heptadecanoyl-2,5-dimethoxytetrahydrofuran (I, b.p. 175–180° (0.05 mm.); calcd. for C₂₃H₄₄O₄: C, 71.83; H, 11.53. Found: C, 72.01; H, 11.50), dotriacontane (m.p. 70–71°; reported¹⁰ m.p. 70.16°) and a mixture of 2,5-dimethoxytetrahydro-2-furyl-bis-hexadecylcarbinol and its dehydration product (b.p. 250–260° (0.05 mm.)).

Hydrolysis of compound I by refluxing for 2 hours with 0.1 *N* hydrochloric acid in 65% aqueous dioxane solution yielded 75% of 3,4-diketoheneicosaldehyde (II, m.p. 45–46° from pentane; calcd. for C₂₁H₃₈O₃: C, 74.51; H, 11.32. Found: C, 74.84; H, 11.33). It gave a negative ferric chloride test and deteriorated rapidly in the presence of moist air or when heated under reduced pressure.

When the time of hydrolysis was extended to 24 hours hydrourushiol (III, isolated as the lead salt¹¹ in 37% yield) was obtained as colorless, waxy crystals, m.p. 57–58° (reported¹¹ m.p. 57.5–

(3) H. Keil, D. Wasserman and C. R. Dawson, *Ann. Allergy*, **4**, 208 (1946).

(4) B. Loev and C. R. Dawson, *THIS JOURNAL*, **80**, 643 (1958).

(5) H. Keil, D. Wasserman and C. R. Dawson, *Science*, **102**, 279 (1945); H. Keil, D. Wasserman and C. R. Dawson, *Ind. Med.*, **14**, 825 (1945).

(6) H. Keil, D. Wasserman and C. R. Dawson, *J. Allergy*, **16**, 275 (1945); W. Cutting and G. Read, *Stanford Med. Bull.*, **16**, 149 (1958).

(7) L. Vargha, J. Ramonczai and P. Bite, *THIS JOURNAL*, **70**, 371 (1948).

(8) J. T. Nielson, N. Elming and N. Clauson-Kaas, *Acta chem. scand.*, **9**, 9 (1955).

(9) N. Clauson-Kaas and F. Limborg, *ibid.*, **6**, 551 (1952).

(10) A. W. Ralston, C. N. Hoerr and L. T. Crews, *J. Org. Chem.*, **9**, 319 (1944).

(11) B. Loev and C. R. Dawson, *THIS JOURNAL*, **78**, 6095 (1956).

58.5°). The infrared spectrum was identical with that of an authentic sample of hydrourushiol.¹²

(12) B. Loev, Dissertation, Columbia University, 1952.

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RECEIVED NOVEMBER 30, 1959

INTERPRETATION OF THE KINETICS OF ACID CATALYZED REACTIONS IN MODERATELY CONCENTRATED AQUEOUS ACIDS¹

Sir:

With reference to the idea² that transition states for some acid catalyzed reactions may contain several molecules of water, one might expect the rate law

$$\text{rate} = k_{\psi} [S] = \frac{k}{K_{SH^+}} [S] h_0 a_{H_2O}^w \frac{f_{SH^+}}{f_{H^+}} \quad (1)$$

and that plots of $(\log k_{\psi} + H_0)$ against $\log a_{H_2O}$ should be linear. Examination of published data on some fifty reactions in 1 to 10*M* hydrochloric, sulfuric and perchloric acids has shown that such plots³ generally are linear. Figure 1 is an example. The slopes vary and are taken to define a new parameter, *w*, characteristic of the reaction.

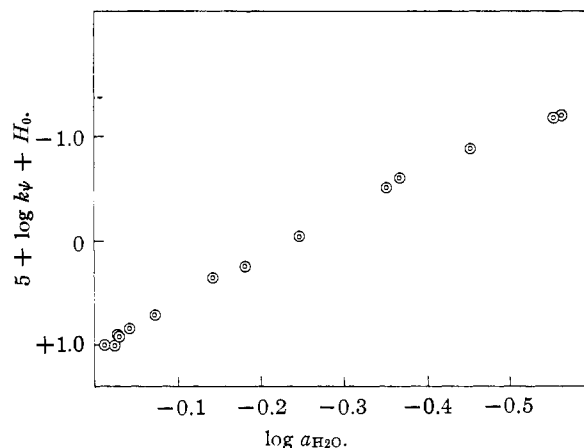


Fig. 1.—Hydrolysis of ethyl acetate in hydrochloric acid solutions; the slope, *w*, is 4.5; data of R. P. Bell, A. L. Dowding and J. A. Noble, *J. Chem. Soc.*, 3106 (1955).

The magnitude of *w* depends on the chemical function of water in the rate determining transition state. When no water is required for transformation of SH⁺ to transition state, as in acetal hydrolyses, *w* is zero or a small negative value. When water acts as a nucleophile (hydrolysis of diethyl ether⁴ or of carboxamides), *w* is about +2. When water functions as a proton transfer agent (enolization of acetophenone⁵), *w* is about +5 to +7.

The size of *w* is thus indicative of mechanism. For example, *w* of ca. +6 for γ -butyrolactone hydrolysis⁶ shows that water acts as a proton

(1) Supported by the Office of Ordnance Research, U. S. Army, and by the National Science Foundation.

(2) J. A. Leisten, *Chemistry & Industry*, 397 (1959).

(3) When S is protonated to an appreciable extent at any acid concentration used, $[\log k_{\psi} - \log \{h_0 / (h_0 + K_{SH^+})\}]$ is plotted against $\log a_{H_2O}$.

(4) J. Koskikallio and E. Whalley, *Can. J. Chem.*, **37**, 788 (1959).

(5) L. Zucker and L. P. Hammett, *THIS JOURNAL*, **61**, 2791 (1939).

(6) F. A. Long, F. B. Dunkle and W. F. McDevit, *J. Phys. Colloid Chem.*, **55**, 829 (1951).

transfer agent in the vital transition state, probably in a general acid catalyzed detachment of the alkoxy "group" from the carbonyl-hydrate ($>C(OH)_2$) of the lactone. For methyl phosphate hydrolysis ($w = +6$)⁷ an analogous mechanism, involving an intermediate with 5-coördinate phosphorus, is implied.

As an empirical criterion of mechanism the above rules promise to succeed the Zucker-Hammett hypothesis,^{5,8} which recently has been sharply criticized. Much of the difficulty stems from the fact that reactions with w values of about -3 to $+3$ all give reasonably straight plots of $\log k_{\psi}$ against $-H_0$, with slope > 1.00 when w is negative and < 1.00 when w is positive. Thus reactions both of the sort in which transformation of SH^+ to transition state requires no water and of the sort in which water is a nucleophile in the slow step (e.g., epichlorohydrin hydrolysis^{8,9}) were classified, by the Zucker-Hammett hypothesis, as being of the former sort. A linear plot of $\log k_{\psi}$ against $\log [HA]$ implies w of about $+6$ and indicates not just water in the transition state, but water acting as a proton transfer agent.

These empirical principles are tempered by theoretical considerations. The theory regards w as closely related to u of equation 1, and broadly indicative of the difference in hydration of transition state *versus* initial state, on a scale set by the "water balance" in determination of H_0 values.¹⁰ This interpretation is supported by the rough parallelism of w with ΔS^* (large positive w is associated with large negative ΔS^* , and *vice versa*), an independent measure of solvent constriction in forming the transition state. Certain deviations from expected w values are intelligible in terms of this theory.

(7) C. A. Vernon, Chem. Soc. London Special Publication No. 8, 1957, p. 17.

(8) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

(9) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959).

(10) K. N. Bascombe and R. P. Bell, *Faraday Soc. Discussions*, **24**, 158 (1957).

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RECEIVED NOVEMBER 23, 1959

THE ALKOXYLATION OF DECABORANE

Sir:

We wish to report the discovery of a novel and useful reaction which first occurred during the attempted iodination of the decaborane anion. The addition of solid iodine to a diethyl ether solution of sodium decaborane resulted in rapid decolorization of the iodine and the precipitation of sodium iodide. Approximately one mole of iodine was employed per mole of sodium decaborane. Work-up of the product under anhydrous conditions afforded an intractable resin, decaborane and a distillable liquid, ethoxydecaborane.

This reaction now has been extended to a series of symmetrical and unsymmetrical ethers, and the reaction conditions optimized. One gram-atom of iodine was employed per mole of sodium decaborane. Yields varied from 13 to 26%. All

products were high boiling, colorless liquids which hydrolyzed rapidly to boric acid. The table summarizes the preparative data obtained from 0.10 mole runs. All products showed proper analyses for C, H and B.

Reactant ROR'	B ₁₀ H ₁₃ OR PRODUCTS R in B ₁₀ H ₁₃ OR	Yield, % ^a
(CH ₃) ₂ O	CH ₃ -	20
(C ₂ H ₅) ₂ O	C ₂ H ₅ -	26
(<i>n</i> -C ₃ H ₇) ₂ O	<i>n</i> -C ₃ H ₇ -	13
(<i>n</i> -C ₄ H ₉) ₂ O	<i>n</i> -C ₄ H ₉	25
C ₆ H ₅ OCH ₃	C ₆ H ₅	15

^a Based on B₁₀H₁₄ consumed.

That phenoxydecaborane was the product of the anisole reaction was shown by the isolation of 2,4,6-tribromophenol from the hydrolysis of the product in bromine water.

The B¹¹ n.m.r. spectra of all the products are similar. It is clear that the 2 and 4 positions have not been attacked; however, the spectra are complicated either by chemical shifts or by substitution in random positions so that it is not possible as yet to state definitely the position of attack. The H¹ n.m.r. spectrum of the ethoxyl derivative is in agreement with the proposed structure.

In diethyl ether solution the alkoxy derivatives displayed absorption maxima at 295 m μ (ϵ 3000) while decaborane absorbs most strongly at 268 m μ under the same conditions.

The infrared spectra of these new derivatives contained B-H bands at 3.90 and 5.25 μ . A strong band near 8 μ was present in all cases and may be associated with the C-O-B system.

The fate of the alkyl group cleaved from the ether reactants has not been determined. No ethane or ethylene could be detected during the preparation of the ethoxyl derivative.

A possible mechanism for these reactions might involve a two electron oxidation of an ether co-ordinated B₁₀H₁₃ anion.

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RECEIVED DECEMBER 9, 1959

CHLOROBIUM CHLOROPHYLL¹

Sir:

All chlorophylls of known structure possess a cyclopentanone ring between C₇ and C₆, with a hydrogen atom and carbomethoxy group at C₁₀, *i.e.*, Ring V. Such pigments and those derivatives which contain an unchanged ring give a positive Molisch phase test, and undergo methanolysis with ring opening.^{2,3} This communication describes a chlorophyll which gives neither of these tests. Furthermore, it is unique in not containing a methoxyl group.

The pigment was obtained from *Chlorobium thiosulfatophilum* (Strain VN)⁴ and was designated

(1) N.R.C. Paper No. 5437.

(2) H. Fischer and A. Stern, "Die Chemie des Pyrrols," Vol. 2 (2), Akademische Verlagsgesellschaft m.b.H., Leipzig, 1940, pp. 48, 242, 330, 313.

(3) H. Fischer and J. Riedmair, *Ann.*, **506**, 107 (1933).

(4) The culture was supplied by Dr. H. Larsen, Norwegian Technical Univ., Trondheim, Norway.