ide[7] gave the hydrocarbon XI identical with a sample of natural isocaryophyllene (kindly provided by Dr. F. Sorm) vapor chromatographically and spectroscopically (infrared, n.m.r.) (C, 88.16; H, 11.74). When the internal elimination of the above hydroxy toluenesulfonate was allowed to proceed for only 15 minutes at 10° and worked up without delay a ketone (XII) isomeric with X was formed which yielded after a Wittig transformation a hydrocarbon (XIII) isomeric with XI (C, 87.75; H, 11.78). This substance, which differs from both caryophyllene and isocaryophyllene clearly must be the unknown *cis–cis* isomer.

Reduction of the hydroxy ketone VII with hydrogen–Raney nickel afforded a mixture of two diols, VIII and IX, in roughly equal amount; these were separated readily by chromatography and VIII could be oxidized back to starting material quantitatively (chromium trioxide–pyridine). The other diol IX (methyl and OH *cis*), m.p. 112.5–113° (C, 74.91; H, 10.76), gave a crystalline mono *p*-toluenesulfonate. m.p. 100.5–101.5°, which was converted by methylsulfinylcarbanion to a bicyclic unsaturated ketone different from the isomers X and XII described above, infrared max. 5.89 μ (C, 81.19; H 10.73). This substance must be the *trans* cycloölefin with *cis* 4-9 fusion since upon prolonged (15 hours) treatment with sodium *t*-butoxide–dimethyl sulfoxide it is isomerized to the ketone XIV, infrared max. 5.89 μ (C, 81.42; H, 10.74), which is transformed by the Wittig process to *d,l*-caryophyllene, identical with natural material spectroscopically and vapor chromatographically (C, 88.04; H, 11.97).

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THE EFFECT OF STRUCTURE AND SOLVENT ON THE RATES OF DEMERCURIZATION. REHYBRIDIZATION OF LEAVING GROUP AS AN IMPORTANT FACTOR IN SOLVOLYSIS REACTIONS[1,2]

Sir:

In previous papers[3] it was demonstrated that alkylmercuric salts undergo loss of mercury to form carbonium ions. By the observed change in kinetic order and rate of solvolysis of ionized and partially ionized alkylmercuric salts with added common ions, it was shown that the material which undergoes decomposition in water solution is the alkylmercuric cation. In less

$$RHgY \rightleftarrows RHg^+ + Y^- \quad (1)$$

$$RHg^+ \longrightarrow R^+ + Hg \quad (2)$$

polar solvents, where the concentration of free ions is low, the reaction apparently occurs largely through the ionized but not dissociated salt.[4]

In accord with our earlier conclusions that these are SN1 reactions, we have found that in acetic acid D-(+)-*sec*-butylmercuric perchlorate (from D-(+)-*sec*-butylmercuric bromide, $[\alpha]_D$ +7.50) gives mostly racemized but partially inverted *sec*-butyl acetate, $[\alpha]_D$ −0.58. (The starting compound is optically stable to the reaction conditions.) Furthermore, *n*-butylmercuric perchlorate gives 16% rearranged acetate. By comparison, *n*-butylamine (amine–nitrous acid reaction) gives 25% rearranged acetate, while primary arylsulfonates yield essentially no rearranged acetate.[5]

Earlier[3] it was shown that the central carbon atom attains a large positive charge in going to the transition state as indicated by the sensitivity of the reaction to change in structure; thus, $k_{t\text{-butyl}}/k_{\text{methyl}} \cong 10^{13}$. These results were explained on the basis of very low susceptibility to nucleophilic attack on carbon. Although these conclusions find support in the rearrangement reported above for the *n*-butyl system, it has been found that the reaction is actually sensitive to changes in nucleophilicity of the solvent. These results can be expressed most conveniently by comparing the effect of α-carbon substitution on the rates of reaction for various leaving groups in different solvents. In Table I,[6] considering as examples the $k_{\text{isopropyl}}/k_{\text{ethyl}}$ ratio differences for mercury and tosylate as leaving groups in acetic and formic acid, the difference in rate for mercury is 10^1 (a factor of ten) and for tosylate $10^{0.6}$ (a rate factor of four). This same general behavior is observed in all examples. (It should be noted that in these considerations it is assumed that solvent interacts equally with the mercuronium groups in each pair of compounds.)

The apparent contradiction that the reaction occurs with low solvent-on-carbon participation, but yet is sensitive to the nucleophilicity of solvent, is explained as follows: in the related tosylate and bromide reactions, the developing positive charge is stabilized by both the leaving group and by nucleophilic participation of solvent. However, with the mercury compounds a significantly different process is occurring. As the mercury–carbon bond is broken, mercury undergoes rehybridization to the $6S^2$ (spherical) configuration and is less able to provide stabilization to the developing carbonium ion. Due to the change in hybridization, the function of the leaving group has become more important and less participation by solvent is required. Therefore, the carbon moiety must obtain stabilization from the groups attached to the central carbon atom, leading to large differences in rate with increasing α-methyl substitution. Similarly, even though the relative amount of nucleophilic participation by solvent

TABLE I

EFFECT OF DEGREE OF α-CARBON SUBSTITUTION ON THE RATES OF SOLVOLYSIS FOR DIFFERENT LEAVING GROUPS IN VARIOUS SOLVENTS

Ratio	Leaving group	HCO_2H	HOAc	EtOH	H_2O
$k_{t\text{-butyl}}$	Hg	...	$10^{5.2}$	$10^{4.2}$	...
$k_{\text{isopropyl}}$	OTs^-	...	...	...	...
	Br^-	...	...	$10^{3.1}$	...
	Hg	$10^{5.6}$	$10^{4.6}$	$10^{2.8}$	$10^{4.3}$
$k_{\text{isopropyl}}$	OTs^-	$10^{2.3}$[c]	$10^{1.7}$[c]	$10^{0.7}$[c]	$10^{1.8}$[d]
k_{ethyl}	Br^-	$10^{1.4}$[e]	...	$10^{-0.12}$[f]	$10^{1.0}$[f]
	Hg	...	$10^{3.1}$	$10^{1.2}$	$10^{2.5}$
k_{ethyl}	OTs^-	$10^{0.2}$[a]	$10^{-0.4}$[a]	$10^{-0.4}$[a]	$10^{-0.02}$[a]
k_{methyl}	Br^-	$10^{0.2}$[b]	...	$10^{-0.4}$[f]	$10^{0.03}$[f]

[a] At 75°, S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). [b] At 95°. I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 173 (1946). [c] At 75°, using the brosylate, from reference in footnote *a*. [d] At 50°, using benzenesulfonate, P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955). [e] At 100°, L. C. Bateman and E. D. Hughes, *J. Chem. Soc.*, 945 (1940). [f] At 50°. S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

(1) Organomercurials. X.

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(3) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477, 4478 (1961). Also, see L. H. Gale, F. R. Jensen and J. A. Landgrebe, *Chem. and Ind.*, 118 (1960).

(4) R. J. Ouellette, Ph.D. Thesis, University of California, 1961.

(5) A. J. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 6233 (1957).

(6) The results reported in this and the next paper were carried out in the indicated solvent in the presence of a small controlled amount of water. All reactions in Table I were carried out using 1 mole equivalent of perchloric acid except for *t*-butyl which was studied utilizing a small amount of acid under pseudo zero order conditions.

may be small, appreciable stabilization of the system is achieved by small variations in the amount of participation.

If the ideas presented here are correct, participation by neighboring groups in demercuration should result in substantial rate enhancements. In accord with these postulates, kinetic evidence for phenyl participation is given in the next paper of this series,[7] and for the norbornylmercuric perchlorates, $k_{exo}/k_{endo} = 1500$.[8]

A reasonable generalization of the ideas presented above is that bond scissions which are accompanied by changes in hybridization can often be expected to exhibit unusual behavior.

An important example of this type of reaction is the amine–nitrous acid reaction; however, the unusual results obtained in this reaction frequently have been ascribed to other factors. The most numerous examples of this type of reaction can be expected to be found in the heterolytic cleavage of carbon–metal bonds in general. It should be noted that this type of reaction probably is encountered frequently in oxidations by many metals having variable valences. Studies are

$$R\text{-}M^{Y} \longrightarrow R^{+} + M^{Y-1} \qquad (3)$$

underway to compare the carbonium ions from alkyllead[9] and related compounds with those from other sources.

(7) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **85**, 367 (1963).
(8) Unpublished results.
(9) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

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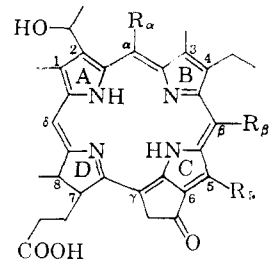
CHLOROBIUM CHLOROPHYLLS. NUCLEAR MAGNETIC RESONANCE STUDIES ON A CHLOROBIUM PHEOPHORBIDE-660 AND -650[1]

Sir:

On the basis of elegant degradative work, the various pheophorbides of both chlorobium chlorophylls-650 and -660 have been assigned structures that are homologs of 2-desvinyl-2-α-hydroxyethyl pyropheophorbide a (I), with a variation among the fractions obtained by partition chromatography apparently resulting from side chains of different lengths on ring B.[2] A detailed investigation of a fraction from chlorobium pheophorbide-660 also led to the assignment of an alkyl substituent (methyl or ethyl) at the δ-methine bridge.[2b]

We have isolated a pure pheophorbide-660, the main fraction from a mixture of chlorobium chlorophylls-660 obtained from a culture of *Chlorobium thiosulfatophilum* (strain PM).[3] Nuclear magnetic resonance studies of this pheophorbide have led to structural evidence which is in most, but not all, aspects complementary to that presented by Holt, *et al.*, for their fraction 5.[2b] Also, from n.m.r. studies, we have made a structural correlation between this pheophorbide-660 and a pheophorbide-650.

The pigments were extracted from dried cells with aqueous acetone, washed into methylene chloride, and precipitated from the concentrated solution with petroleum ether. The mixture of chlorophylls was washed with petroleum ether and dissolved in ether to



I. $R_5 = CH_3$, $R\alpha = R\beta = H$
Ia, $R_5 = CH_3$ (or C_2H_5)
$R\beta = C_2H_5$ (or CH_3), $R\alpha = H$, or
$R\beta = H$, $R\alpha = C_2H_5$ (or CH_3)

which concd. hydrochloric acid then was added. After being stirred at room temperature under argon for one hour, the solution was evaporated *in vacuo* to remove the ether and was passed through a column of powdered polyethylene.[4] The effluent pheophorbides were extracted into methylene chloride and precipitated from the concentrated solution by adding petroleum ether; yield, *ca.* 5% from dried cells.[5]

The mixture of pheophorbides was partitioned on powdered polyethylene with 75% aqueous methanol.[6] Paper chromatography of the acids isolated from chromic acid oxidations indicated the presence of methyl (acetic acid) and ethyl (propionic acid) substituents in the main fraction. Later fractions gave butyric acid and valeric acid(s). The main fraction Ia, after rechromatography on polyethylene, was homogeneous by thin layer chromatography and had the following properties: *Anal.* Calcd. for $C_{35}H_{40}N_4O_4 \cdot H_2O$[7]: C, 70.2; H, 7.1; N, 9.4; C–CH_3, 7/599. Found: C, 70.4; H, 6.6; N, 9.4; C–CH_3, 5.6/599. Visible and ultraviolet absorption: $\lambda_{max}^{CH_3OH}$ 667 mμ (ϵ 43,000), 610 (7,400), 553 (12,500), 517 (8,300), 485 (2.700), 410 (102,000), 330 (26,200); infrared absorption: $\nu_{max}^{CHCl_3}$ 3090, 1715, 1675 cm.$^{-1}$. With diazomethane, the methyl pheophorbide-660, was formed; infrared absorption: $\nu_{max}^{CHCl_3}$ 3060, 1737, 1690 cm.$^{-1}$; *Anal.* Calcd. for $C_{36}H_{42}N_4O_4$: C, 72.7; H, 7.1; N, 9.4; OCH_3, 5.2; Found. C, 72.9; H, 7.8; N, 9.3; OCH_3, 4.8.

The n.m.r. spectrum[8] of Ia showed absorption at these δ values (p.p.m., TMS = 0): one proton singlet at 9.67 (10.01) and 9.34 (9.49) assigned to bridge methine hydrogens,[9-11] a one proton multiplet at 6.10 (6.58) assigned to the alpha hydrogen of a hydroxyethyl group,[10] a two proton singlet at 4.92 (5.33) assigned to a cyclopentenone methylene,[10,11] and three singlets at 3.33 (3.28), 3.40 (3.50), 3.75 (3.84) assigned to methyls attached to the macrocyclic aromatic ring.[10,11] After acetylation of Ia, the multiplet at 6.10 now appeared at 7.25. Reduction of Ia with borohydride caused a hypsochromic shift of the 410 and 667 mμ peaks to 396 and 647 mμ, respectively, removed the 1675 cm.$^{-1}$ infrared absorption, and replaced the two-proton singlet at 4.92 in the n.m.r. spectrum with a new multiplet under the existing absorption at 6.10. Treatment of Ia with ethoxide in C_2H_5OD removed the signal at 4.92; similar treatment in ethanol restored this signal. Treatment of Ia with warm CH_3COOD for three hours[9] removed the *lower* field, 9.67, methine

(1) This work was sponsored in part by Grant A1-0488 from the National Institutes of Health, United States Public Health Service.

(2) (a) A. S. Holt and H. V. Morley, *J. Am. Chem. Soc.*, **82**, 500 (1960); (b) A. S. Holt, D. W. Hughes, H. J. Kende and J. W. Purdie, *ibid.*, **84**, 2835 (1962); (c) D. W. Hughes and A. S. Holt, *Can. J. Chem.*, **40**, 171 (1962); (d) A. S. Holt and D. W. Hughes, *J. Am. Chem. Soc.*, **83**, 499 (1961); (e) H. V. Morley and A. S. Holt, *Can. J. Chem.*, **39**, 755 (1961).

(3) R. Y. Stanier and J. H. C. Smith, *Biochem. Biophys. Acta*, **41**, 478 (1960); H. Rapoport and H. P. Hamlow, *Biochem. Biophys. Res. Commun.*, **6**, 134 (1961).

(4) We wish to thank the Dow Chemical Co. for a gift of powdered polyethylene.

(5) The technical assistance of Mr. F. Cahn in this isolation we gratefully acknowledge.

(6) M. Calvin and A. F. H. Anderson, *Nature*, **194**, 285 (1962).

(7) Dehydration at 80° (0.1 mm.) results in partial alteration.

(8) N.m.r. spectra were taken in $CDCl_3$ and $CDCl_3$–CD_3OD; those taken in the latter solvent are given in parentheses.

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(10) E. D. Becker, R. B. Bradley and C. J. Watson, *ibid.*, **83**, 3743 (1961).

(11) W. S. Caughey and W. S. Koski, *Biochem.*, **1**, 923 (1962).