for the relative rates of abstraction of halogen atoms from alkyl halides by methyl radicals. These reactivities are closely parallel to each other, and different from those for SN1 reactions. One example is provided by the fact that benzyl bromide is more reactive than *t*-butyl bromide in the reduction, whereas *t*-butyl chloride solvolyses faster than benzyl chloride by a factor which depends strongly on the solvent.[9] The high reactivity of carbon tetrachloride (72.4), comparable to benzyl bromide (33.5), constitutes another.

The reactivity sequence bromide < iodide is shown by the fact that *n*-heptyl iodide is more reactive than *n*-butyl bromide by a factor of 65.

The data presented here are consistent with a mechanism in which the rate of formation of an alkyl free radical is the prime factor in determining reactivity of a halide. This might involve a chain mechanism in which an organotin radical abstracts a halogen atom from the halide in one step, and the resulting alkyl radical abstracts a hydrogen atom from the organotin hydride in the other step.[10]

Catalysis of the reaction by azobisisobutyronitrile confirms the existence of a chain mechanism: tri-*n*-butyltin hydride in toluene at 80 ± 2° reduced benzyl chloride, chlorocyclohexane, and bromobenzene to the extents of 100, 70, and 41% in 35 min. in the presence of 1.5 mole % of the catalyst, and to the extents of 26, 1, and 5% in its absence.

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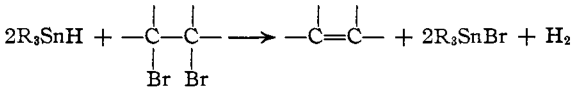
[9] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 616 (1956).

[10] This last statement cannot, of course, apply to the dehalogenation of vicinal dihalides, which proceeds according to the equation



$$2R_3SnH + -\underset{Br}{\underset{|}{\overset{|}{C}}}-\underset{Br}{\underset{|}{\overset{|}{C}}}- \longrightarrow -\overset{|}{C}=\overset{|}{C}- + 2R_3SnBr + H_2$$

[11] National Science Foundation Senior Postdoctoral Fellow, California Institute of Technology, 1959–1960.

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RECEIVED AUGUST 2, 1962

THE DECOMPOSITION OF SULFUR YLIDS TO CARBENES[1]

Sir:

Franzen and co-workers[2] recently studied the reaction of alkyldiphenyl-sulfonium salts with strong bases. On the basis of isolating triphenylmethane (42%), 1,1,1-triphenylpentane (15%) and 1-butene (7%) from the reaction of tritylsodium with *n*-butyldiphenylsulfonium tetrafluoroborate (Ia) they postulated that this salt was first converted to the corresponding ylid (IIa) (by proton abstraction) which then decomposed to phenyl sulfide and the carbene (IIIa). Similar results were reported for the benzyldiphenylsulfonium salt (Ib), affording 1,1,1,2-tetraphenylethane by an insertion reaction of the carbene (IIIb) with triphenylmethane. However, all attempts to trap the carbene intermediates with cyclohexene were unsuccessful. In fact, none of their products[3] require the postulation of carbenes as reaction intermediates. They can be accounted for by displacement and/or elimination reactions.

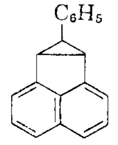
In our original work[1] on the chemistry of dimethylsulfoniumfluorenylide we obtained several products which were best accounted for by the ylid first decomposing to a carbene. We have now succeeded in demonstrating conclusively that sulfur ylids can be decomposed to carbenes by trapping the carbene formed from the ylid (IIb). Franzen and Wittig[4] previously reported the decomposition of trimethylammoniummethylide to methylene which was trapped with cyclohexene to form norcarane.

$$\mathrm{R{-}CH_2{-}\overset{+}{S}(C_6H_5)_2} \quad \rightarrow \quad \underset{\mathrm{II}}{\mathrm{R{-}\overset{-}{C}H{-}\overset{+}{S}(C_6H_5)_2}} \rightarrow$$

$$\mathrm{Ia,\ R = C_3H} \qquad\qquad \underset{\mathrm{III}}{\mathrm{R{-}CH{:}}} + \mathrm{(C_6H_5)_2S}$$
$$\mathrm{Ib,\ R = C_6H_5}$$

Addition of 4 mmoles of *n*-butyllithium solution to a slurry of 4.0 mmoles each of benzyldiphenylsulfonium tetrafluoroborate (Ib) and acenaphthylene in anhydrous tetrahydrofuran at −40° afforded 4.0 mmoles of lithium tetrafluoroborate (100%); 3.3 mmoles of phenyl sulfide (83%), determined and identified by oxidation to phenylsulfone, m.p. 122.5–124.5 (lit.,[5] m.p. 124°); 1.1 mmoles of unreacted acenaphthylene; and 1.2 mmoles of 7-phenyl - 7H - 6b,7a - dihydrocycloprop[a]acenaphthylene (IV) (43% based on unreacted acenaphthylene, 31% based on Ib), m.p. 170° dec.

The adduct (IV) was identified by its inertness to cold permanganate or bromine; by its infrared spectrum (no olefinic absorption, λ_{max} 13.70 and 14.83 μ, characteristic of monosubstituted aryl); by its ultraviolet spectrum (λ_{max} 232 mμ (log ϵ 4.3), 296 (3.6), 310 (3.5) and 323 (3.1)); and by oxidation with chromic acid to benzoic acid (m.p. 120–121°) and naphthalene-1,8-dicarboxylic acid anhydride, m.p. 272.5–274° (lit.,[6] m.p. 274), identified by admixture melting point and infrared spectra comparison with an authentic sample.



IV

We have found that other alkyldiphenylsulfonium ylids can be decomposed to carbenes which can be trapped with acenaphthylene and other olefins. We have also noted that this decomposition can be avoided by working at even lower temperatures. This work is continuing and will be published in detail at a later date.

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[1] This is paper VII of our series "The Chemistry of Ylids"; for paper VI see Johnson and LaCount, *J. Am. Chem. Soc.*, **83**, 417 (1961).

[2] V. Franzen, H. J. Schmidt and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961).

[3] An unspecified amount of a (β-phenylisopropyl)-ethyl ether resulting from an insertion reaction of (possibly) the benzyl carbene on ethyl ether was reported and identified by vapor phase chromatography analysis and infrared spectrum.

[4] V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

[5] O. Hinsberg, *Chem. Ber.*, **43**, 290 (1910).

[6] C. Graebe and E. Gfeller, *ibid.*, **25**, 652 (1925).

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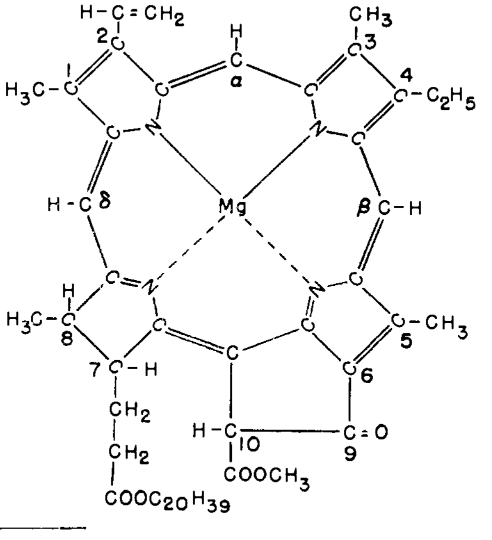
SITE OF EXCHANGEABLE HYDROGEN IN CHLOROPHYLL *a* FROM PROTON MAGNETIC RESONANCE MEASUREMENTS ON DEUTERIO-CHLOROPHYLL *a*[1]

Sir:

As shown by an indirect infrared method, chlorophyll *a* possesses one slowly exchangeable hydrogen atom when the chlorophyll is treated with methanol in carbon tetrachloride solution at room temperature in the dark.[2] Although the position of the exchangeable hydrogen could not be established by the exchange method, considerations had indicated that the active hydrogen probably was located at the C-10 position (I).[3]

We have now carried out proton magnetic resonance measurements (Varian A-60 n.m.r. spectrometer equipped with an audio oscillator and counter) that confirm the presence of but one exchangeable hydrogen atom in chlorophyll *a* (under our exchange conditions). The exchangeable hydrogen is not located at the C-10 position, but is in fact on the δ-bridge carbon atom of the porphyrin ring (I). The n.m.r. observations were made with two materials; not only was the exchange followed in ordinary chlorophyll *a*, but also in the fully deuteriated chlorophyll *a* that we have available.[4] The use of the deuterio-chlorophyll made it possible to detect hydrogen resonances that might otherwise have been obscured in ordinary chlorophyll.



Chlorophyll *a*, isolated from spinach and carefully purified, exhibited three sharp, low field resonance bands ($\tau = 0.62, 0.85$, and 1.81, measured in $CDCl_3$, tetramethylsilane as internal indicator). These bands correspond to the three bands found in chlorin e_6 trimethyl ester and assigned to the α-, β- and δ-bridge hydrogen atoms by Woodward and Skaric.[5] All other hydrogen resonances in chlorophyll *a*, including the C-10 hydrogen, lie at higher fields. When chlorophyll *a* was treated with excess CH_3OD in CCl_4 for 48 hours,[2] the band at $\tau = 1.81$ disappeared, in a manner entirely analogous to that reported for chlorin by Woodward and Skaric.[5] When the exchanged chlorophyll *a* was treated with CH_3OH, the band reappeared. These facts indicate that the δ-bridge hydrogen atom undergoes the exchange.

To minimize uncertainties and ambiguities in the interpretation of the very complex chlorophyll n.m.r. spectrum, we followed the hydrogen exchange in deuterio-chlorophyll *a*.[4] This substance showed no proton resonances. On treatment with CH_3OH in CCl_4 for 48 hours, one, and only one, proton resonance appeared at $\tau = 1.81$. Again, treatment with CH_3OD caused the resonance peak to disappear. These results with deuterio-chlorophyll *a* demonstrate unequivocally that only one hydrogen atom undergoes exchange under the reaction conditions used here, and that the labile hydrogen is located on the porphyrin ring at the δ position.

The remarkable observations of Woodward and Skaric[5] on the chemical and exchange behavior of chlorins thus also appear to be valid for chlorophyll *a* itself. That the hydrogen at the δ position is more labile than the one at C-10 could only be established by measurements on chlorophyll itself rather than on derivatives lacking the central magnesium atom and the cyclopentanone ring. Although the conditions used for the hydrogen exchange are certainly not physiological, nevertheless the lability of the δ-hydrogen atom in chlorophyll *a* as established here may also be pertinent to the chemical behavior of chlorophyll *a* in photosynthesis.

We are deeply indebted to Dr. Gerhard L. Closs of the University of Chicago for guidance and instruction in the interpretation of the n.m.r. spectra.

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. J. Katz, M. R. Thomas, H. L. Crespi and H. H. Strain, *J. Am. Chem. Soc.*, **83**, 4180 (1961).

[3] H. Fischer and S. Goebel, *Ann.*, **522**, 168 (1936); S. Aronoff, *Encyclopedia of Plant Physiology*, **5**, 234 (1960); W. Vishniac and I. A. Rose, *Nature*, **182**, 1089 (1958).

[4] H. H. Strain, M. R. Thomas, H. L. Crespi, M. I. Blake and J. J. Katz, *Ann. New York Acad. Sci.*, **84**, 617 (1960).

[5] R. B. Woodward and V. Skaric, *J. Am. Chem. Soc.*, **83**, 4676 (1961).

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THE EFFECT OF H_2O ON THE γ-RADIOLYSIS OF AERATED CH_3OH[1]

Sir:

We wish to report a previously overlooked[2] effect of H_2O on the γ-radiolysis of aerated methanol which gives promise of serving as a useful tool in the study of radiolytic mechanism.

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[1] Research performed under the auspices of the United States Atomic Energy Commission.

[2] E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3970 (1961).