square root of the slope of the C_2D_6 appearance curve at a given CD_3NO pressure and assumption of the above mechanism leads to an estimate for $k_4/k_6^{1/2}$ of 2.5×10^{-9} [cm.^{3}/molecule-sec.]$^{1/2}$. Combining this ratio with the value[15] of 7.5×10^{-11} cm.^{3}-molecule^{-1}-sec.$^{-1}$ for k_6 yields a value for k_4 of 2.2×10^{-14} cm.^{3}-molecule^{-1}-sec.$^{-1}$. If we take the third-order rate constant[11] of 8.8×10^{-31} cm.^{6}-molecule^{-2}-sec.$^{-1}$ for equation 1' and assume azomethane to be as effective a third body as acetone, we are led to the interesting conclusion that, at 25° and 12 mm. pressure, nitric oxide is only 15 times more effective than nitrosomethane in scavenging methyl radicals.

Acknowledgment.—This work was supported in part by Petroleum Research Fund Grant 833-A1, and in part by Contract AF33(616)7716 with Office of Aerospace Research. A more complete report shall be forthcoming.

(15) R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.*, **19**, 85 (1951).

DEPARTMENT OF CHEMISTRY   A. MASCHKE
WHITMORE LABORATORY   B. S. SHAPIRO
THE PENNSYLVANIA STATE UNIVERSITY   F. W. LAMPE
UNIVERSITY PARK, PENNSYLVANIA
                    RECEIVED MAY 3, 1963

Prostaglandins and Related Factors. 17.[1]
The Structure of Prostaglandin E_3[2]

Sir:

The chemical structure (Fig. 1) of prostaglandin E_1 (PGE$_1$) has been reported.[3] Recently, two new biologically active compounds were isolated from sheep vesicular glands and subjected to structural analysis.[4]
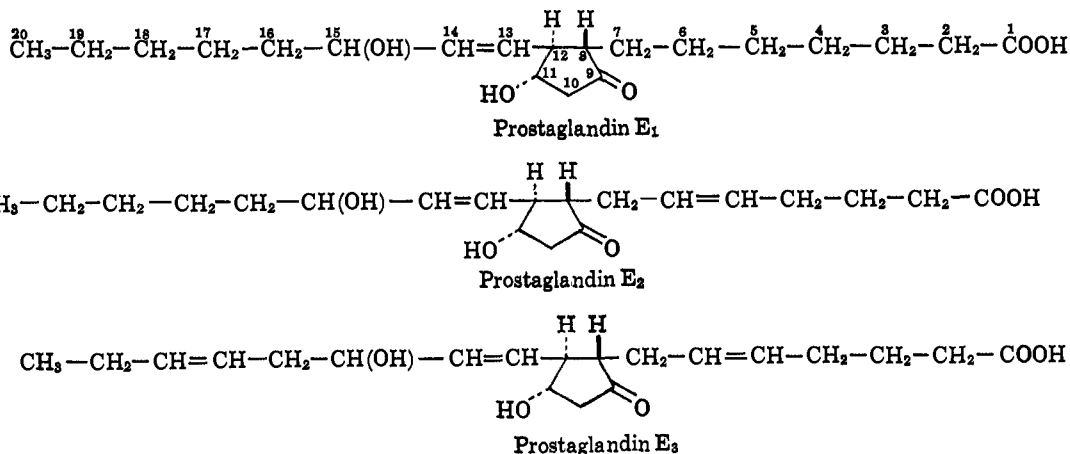
This led to elucidation of the structure of prostaglandin E_2 (PGE$_2$) (Fig. 1) and afforded the following data on prostaglandin E_3 (PGE$_3$).

Mass spectrographic analysis of the methyl ester of PGE$_3$ demonstrated that its molecular weight is two units less than that of PGE$_2$ and four units less than that of PGE$_1$. That the parent structure is the same for all three compounds followed from their conversion by catalytic reduction into the same derivative as judged by mass spectrographic analysis. The presence of two of the three double bonds of PGE$_3$ in the same positions as in PGE$_2$ was demonstrated by analysis of the mass spectra of all three compounds, by isolation of glutaric acid after chromic acid oxidation of both PGE$_2$ and PGE$_3$ and, finally, by the appearance of the same chromophore

$$R'\!\!-\!\!\langle\!\!=\!\!\rangle\!\!-CH=CH-R''$$
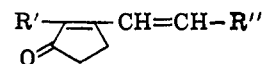
$(\lambda_{max}^{EtOH}\ 278\ m\mu)$ on treatment of PGE$_1$, PGE$_2$ or PGE$_3$ with alkali.[4]

A detailed analysis of the mass spectrum of PGE$_3$ further indicated that the third double bond in this compound is located in the terminal pentyl group.[4] The present report is concerned with nuclear magnetic resonance studies, which in combination with the mass spectrographic analyses unequivocally demonstrate the structure of prostaglandin E_3.

The n.m.r. spectra were determined with a Varian A-60 spectrophotometer on deuteriochloroform solutions of the methyl esters containing tetramethylsilane as standard. The n.m.r. spectrum of the methyl ester of PGE$_3$ is shown in Fig. 2.

Figure 1.

Six olefinic protons give rise to signals between 4.25 and 4.8 τ. Two of these protons appear at lower frequencies (4.25–4.5 τ) and in the same region as the two olefinic protons in PGE$_1$. The other four olefinic protons in PGE$_3$ have approximately the same chemical shift as the protons attached to the double bonded carbon atoms in the carboxyl side chain of PGE$_2$.
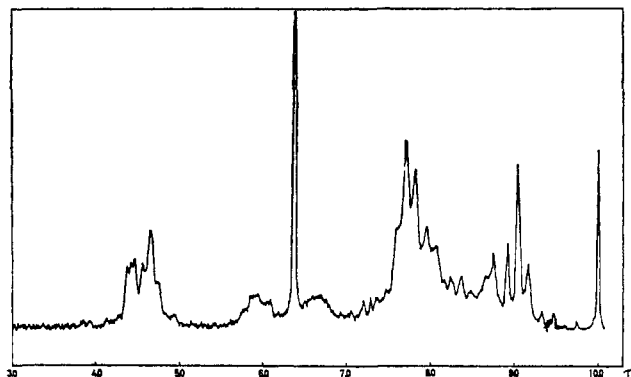

Fig. 2.—Proton n.m.r. spectrum of the methyl ester of prostaglandin E_3.

(1) The prostaglandins belong to a new class of physiologically highly active compounds having smooth muscle stimulating and blood pressure depressing activity. For pertinent references, see S. Bergström and B. Samuels-

son, *J. Biol. Chem.*, **237**, PC 3005 (1962). According to the nomenclature recently introduced (S. Bergström, R. Ryhage, B. Samuelsson and J. Sjövall, *ibid.*, in press) the parent C$_{20}$ acid is called prostanoic acid and prostaglandin E$_1$, 11α,15-dihydroxy-9-keto-prost-13-enoic acid and prostaglandin E$_3$, 11α,15-dihydroxy-9-keto-prosta-5,13-dienoic acid. X-Ray diffraction studies (S. Abrahamsson, S. Bergström and B. Samuelsson, *Proc. Chem. Soc.*, 332 (1962)) of a derivative of prostaglandin E$_1$ have provided the stereochemical features shown in Fig. 1.

(2) This study has been supported by grants to Professor Sune Bergström from "Statens Medicinska Forskningråd" and "Knut och Alice Wallenbergs Stiftelse."

(3) S. Bergström, R. Ryhage, B. Samuelsson and J. Sjövall, *Acta Chem. Scand.*, **16**, 501 (1962).

(4) S. Bergström, F. Dressler, R. Ryhage, B. Samuelsson and J. Sjövall, *Arkiv Kemi*, **19**, 563 (1962).

The hydroxyl groups at C-11 and C-15 are recognized as broad bands within the range 5.6–7.0 τ, which shift on dilution. The carbon bounded hydrogens in these positions appear between 5.6 and 6.2 τ and the protons of the carbomethoxy group are superimposed on this region with a sharp peak at 4.37 τ. The n.m.r. spectra of PGE_1 and PGE_2 exhibit essentially the same absorption pattern at these frequencies.

Of particular interest is the absorption due to the protons of the methyl group (C-20) which appears as a clear triplet at 9.05 τ and with a coupling constant of 7 c.p.s., whereas corresponding groups in PGE_1 and PGE_2 appear as relatively sharp peaks at 9.10 τ flanked by broad bands. The spin–spin splitting and chemical shift of the methyl protons in PGE_3 demonstrate that the double bond in the terminal pentyl group is located between C-17 and C-18. The same pattern for the methyl protons has been observed for methyl linolenate,[5] methyl densipolate[6] and other fatty acids containing a double bond in β,γ-position to the terminal methyl group.[5]

The data also exclude the presence of a double bond between C-16 and C-17 or between C-18 and C-19. In the former case the olefinic protons would appear at lower frequency due to the hydroxyl group at C-15, and in the latter case the methyl protons would appear as a doublet at lower frequency. The structure of prostaglandin E_3 ($11\alpha,15$-dihydroxy-9-keto-prosta-5,13,17-trienoic acid) is shown in Fig. 1.

(5) W. H. Storey, Jr., *J. Am. Oil Chemists' Soc.*, **37**, 676 (1960).

(6) C. R. Smith, Jr., T. L. Wilson, R. B. Bates and C. R. Scholfield, *J. Org. Chem.*, **27**, 3112 (1962).

DEPARTMENT OF CHEMISTRY
KAROLINSKA INSTITUTET   BENGT SAMUELSSON
STOCKHOLM, SWEDEN

The Molecular Structure of i-$B_{18}H_{22}$

Sir:

We have established by three dimensional X-ray diffraction methods the chemical composition and molecular structure of a new boron hydride, i-$B_{18}H_{22}$. This is the first example of isomers among the known boron hydrides. The relation of the structure of i-$B_{18}H_{22}$ to the previously described[1] $B_{18}H_{22}$ structure is shown as I and II, respectively, in Fig. 1.

i-$B_{18}H_{22}$ appears as a lesser product of the reaction[2] which produces $B_{18}H_{22}$ from the $B_{20}H_{18}{}^{-2}$ ion.[3] A total of 3206 independent X-ray diffraction maxima were obtained from about 10,000 observations on single crystals. The unit cell is monoclinic, of symmetry $P2_1/c$, and has parameters $a = 9.199 \pm 0.002$, $b = 13.180 \pm 0.001$, $c = 12.515 \pm 0.002$ and $\beta = 109°35'$. The measured density of 1.003 g./cm.³ requires four molecules per unit cell and yields the calculated molecular weight 215.7 in good agreement with the value 216.8 for the formula $B_{18}H_{22}$. Aside from anisotropic thermal parameters for B, isotropic thermal parameters for H and a single scale factor, there are 54 position parameters for B and 66 position parameters for H which were then determined by the 3206 observations.

The boron arrangement was solved by simultaneous multiple superposition procedures[4,5] following a detailed

(1) P. G. Simpson and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **48**, 1490 (1962); *J. Chem. Phys.*, in press.

(2) A. R. Pitochelli and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3218 (1962).

(3) A. Kaczmarczyk, R. D. Dobrott and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U.S.*, **48**, 729 (1962).

(4) P. G. Simpson and W. N. Lipscomb, Abstracts, American Crystallographic Association Meeting, Cambridge, Massachusetts, April 28–30.

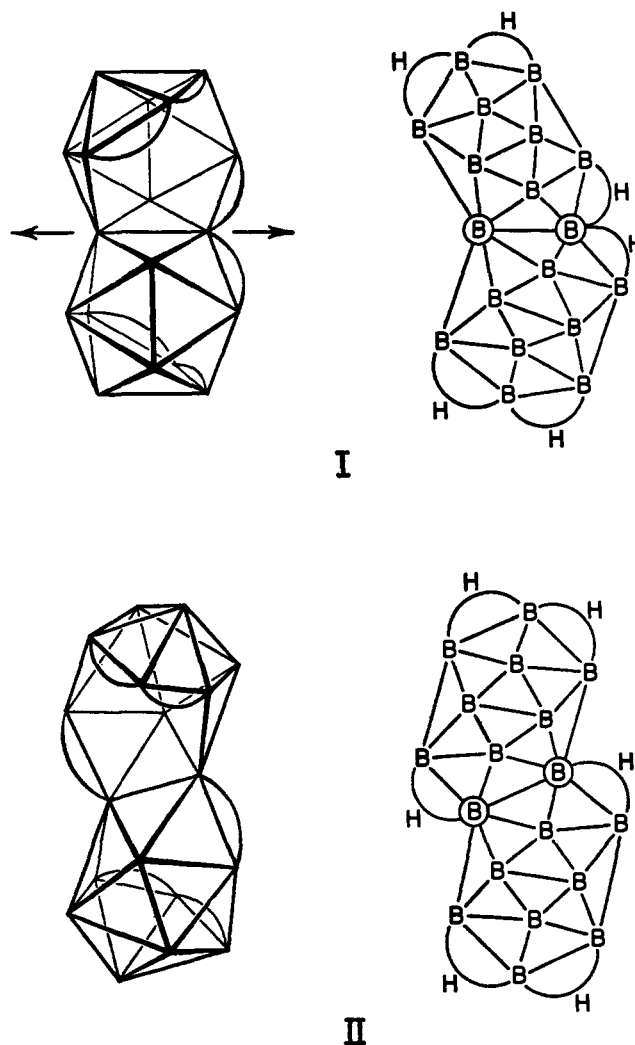(5) P. G. Simpson, R. D. Dobrott and W. N. Lipscomb, to be published.

Fig. 1.—Comparison of structures of i-$B_{18}H_{22}$ (I) and $B_{18}H_{22}$ (II). The former has a twofold axis indicated by arrows, whereas the latter has a center of symmetry. One terminal H atom has been omitted from each B atom except for the encircled B atoms which do not have terminal H atoms. The two bridge H atoms to the circled B in I are considerably above and below the plane of the drawing, and hence do not present a steric problem. The most positively charged B atom is the circled B atom attached to two bridge H atoms in I.

analysis of the symmetry minimum function[5] derived from the sharpened three-dimensional Patterson function. No assumptions were made about the number or positions of the H atoms all of which were located uniquely from three-dimensional electron density maps from which the B atoms had been subtracted. Thus these methods also provide a determination of the chemical formula. At the present state of refinement the value of $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$ is 0.10 for all observed reflections.

The structures of i-$B_{18}H_{22}$ and $B_{18}H_{22}$ (Fig. 1) may be described as decaborane-14 cages joined by atoms in common at the 5–6 positions (the circled B atoms) in such a manner that the cages open up in opposite directions. The manner of joining is 5 in common with $5'$ (*i.e.*, 5–5') and 6–6' in i-$B_{18}H_{22}$, which has a twofold axis of symmetry, and 5–6' and 6–5' in $B_{18}H_{22}$, which has a center of symmetry. Each of the B atoms except those which are circled has a terminal H atom, which is not shown in the diagram.

A theoretical study of the charge distribution in i-$B_{18}H_{22}$ is being undertaken in order to provide a basis for prediction of its nucleophilic and electrophilic