

Bu_2BCF_3 or some more complex system containing B-CF₃ bonds. The filtered solution was evaporated, leaving a viscous, non-volatile liquid which would not react with $(\text{CH}_3)_3\text{N}$. However, it did react with BF_3 producing the volatile compounds BuBF_2 and CF_3BF_2 . Alternatively, KBBu_2 could be made as a solution in $(\text{C}_2\text{H}_5)_3\text{N}$. Treatment with CF_3I , evaporation of the solvent and reaction of the product with dry HCl gave the presumed Bu_2BCF_3 . This could be distilled under vacuum at room temperature (along with Bu_3B and other impurities) and again converted by BF_3 to CF_3BF_2 and BuBF_2 . Evidence of the formula of CF_3BF_2 was the vapor-phase mol. wt. value 117.5 ± 1.5 (calcd. 117.8) and its formation of 1:1 adducts with $(\text{CH}_3)_3\text{N}$ and $(\text{C}_2\text{H}_5)_3\text{N}$, with recovery by action of dry HCl . Catalysts such as O_2 and glyptal resin caused its quantitative conversion to BF_3 and a white polymer, presumed to be $(\text{CF}_2)_n$. Fusion with potassium metal⁴ and spectrophotometric analysis of the resultant soluble fluoride⁵ gave 5.1F per CF_3BF_2 .

The Southern California (USC) approach was based on the idea that a $\text{CF}_3\text{-S}$ compound might attack a boron hydride to form H-S and B-CF₃ bonds. The disulfide CF_3SSCF_3 ⁶ proved to be inert toward diborane, but could be used to make CF_3SCl ,⁷ and this reacted well enough with diborane during 15-18 hr. in sealed Pyrex containers at 60°. The ratio 2.1 CF_3SCl per B_2H_6 seemed optimal for the desired product, which was easily separable from the accompanying H_2 , BF_3 , B_2H_6 and non-volatile white solids but not from CF_3SH and CF_3SSCF_3 . A 0.658 mmole fraction (6 mm. at -78°), having average mol. wt. 126.8, reacted with 0.446 mmole of $(\text{CH}_3)_2\text{O}$ to form a slightly volatile solid adduct, leaving 0.212 mmole of mixed CF_3SH and CF_3SSCF_3 , average mol. wt. 144.4. Hence the boron compound had mol. wt. 118.4 (calcd. for CF_3BF_2 , 117.8) and had formed a 1:1 etherate. Weighed etherate samples, hydrolyzed with NaOH , yielded neither Cl^- nor any sulfur compound; moreover, the recovered ether, the acid-liberated CO_2 and the titrated boric acid all corresponded to the formula $(\text{CH}_3)_2\text{O} \cdot \text{CF}_3\text{BF}_2$. However, the fluoride analysis (method successful for $\text{Et}_2\text{O} \cdot \text{BF}_3$) gave one-third to one-half of the expected 5F per mole. A complicated mass spectrum for the etherate included CF_3^+ (69, strong), possible BF (29 + 30), possible BF_2 (48 + 49) and CF_2 (50). The infrared spectrum of the etherate

(satd. vapor at 25°, meter-length cell) showed C-H stretching as a composite peak at 2800 cm^{-1} , C-F stretching in the range 1160-80 and peaks at 1100 and 1115 possibly showing B-F stretching; other features were indistinct.

In the presence of mercury CF_3BF_2 slowly formed BF_3 and non-volatile white solids. An unstable anisole complex could be made, but diphenyl ether was inert. Trimethylamine displaced $(\text{CH}_3)_2\text{O}$ from the etherate, but BF_3 would not remove this ether, suggesting that CF_3BF_2 is a stronger Lewis acid than BF_3 , as theory would demand.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

THERAN D. PARSONS
EVERETT D. BAKER

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIFORNIA

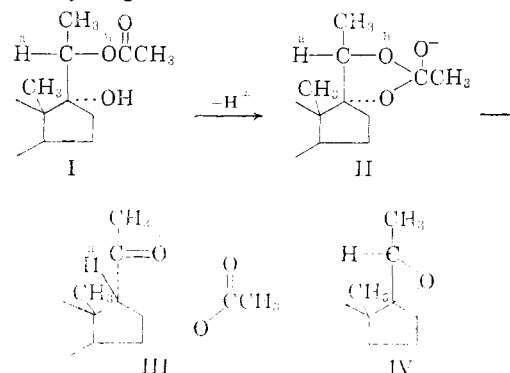
ANTON B. BURG
GORDON L. JUVINALL

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MECHANISM OF THE SERINI REACTION

Sir:

The Serini reaction¹ consists in refluxing a *vic*-diol monoacetate of type I with zinc dust in toluene and results in formation of the ketone III. The possibility that the reaction involves the 17,20-olefin was considered and experimentally eliminated by one of us and Huang-Minlon.² Shoppee's suggestion³ that a 17,20-oxide is an intermediate was questioned by Wagle,⁴ who found that under the conditions of the Serini reaction cholestane-3 β ,5 α ,6 β -triol 3,6-diacetate is converted to 3 β -acetoxycholestane-6-one whereas the 3 β ,5 α ,6 β -triol 3,6-diacetate is not. Wagle suggested a mechanism involving formation of the intermediate cyclic orthoacetate anion II and cleavage, with a 1,2-shift of hydrogen, to the ketone III and acetate ion.



For clarification of the mechanism, we prepared these compounds and subjected each of them to the Serini reaction: 20 β -deuterio- Δ^5 -pregnene-3 β ,17 α ,20 α -triol 3,20-diacetate (Ia), 20 α -O¹⁸- Δ^5 -pregnene-3 β ,17 α ,20 α -triol 3,20-diacetate (Ib), and 3 β - α -(tetrahydropyranoxy)-17 α ,20-oxido- Δ^5 -pregnene (IV). The results all support the Wagle mechanism: 20 β -H migrates to C₁₇ with inversion at this site; C₂₀-O- changes to C₂₀=O; the 17,20-oxide IV does not function as an intermediate.

(1) A. Serini, W. Logemann and W. Hildebrand, *Ber.*, **72**, 391 (1939).

(2) L. F. Fieser and Huang-Minlon, *J. Am. Chem. Soc.*, **71**, 1840 (1949).

(3) C. W. Shoppee, *J. Chem. Soc.*, 1671 (1949).

(4) S. S. Wagle, Dissertation, Harvard University, 1949.

(4) P. J. Elving and W. B. Ligett, *Ind. Eng. Chem., Anal. Ed.*, **14**, 449 (1942).

(5) R. J. Bertolacini and J. E. Barney II, *Anal. Chem.*, **30**, 202 (1958).

(6) G. A. R. Brandt, H. J. Emelús and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

(7) The process $\text{CF}_3\text{SSCF}_3 + 5.3\text{NH}_3 \rightarrow \text{H}_3\text{NSCF}_3 +$ brown solids, occurring easily (or even explosively if not controlled) in liquid ammonia above -77°, was described by G. L. Juvinall, M.Sc. Thesis, USC Libraries, 1956, p. 9. The then-new compound H_3NSCF_3 was converted by HCl to CF_3SCl , as later reported by H. J. Emelús and S. N. Nabi, *J. Chem. Soc.*, 1103 (1960); thus CF_3SCl was made more conveniently than by the earlier photochemical method of R. N. Haszeldine and J. M. Kidd, *ibid.*, 3219 (1953). Later $(\text{CH}_3)_3\text{NH}$ and CF_3SSCF_3 were used to make $(\text{CH}_3)_3\text{NSCF}_3$ for the same purpose. The vapor tensions of $(\text{CH}_3)_3\text{NSCF}_3$ (after reflux-fractionation at 0° to remove H-bonded amine, which persisted at lower temperatures) conformed to the equation $\log p_{\text{mm}} = 5.40514 - 0.004569T + 1.75 \log T - 1783/T$ (78.25 mm. at 0°; b.p. 55.7°; Trouton constant, 21.4 cal./deg. mole).

Reduction of 17 α -hydroxypregnenolone diacetate with lithium aluminum deuteride and then acetylation afforded Ia, m.p. and mixed m.p. with the H-analog 198–201.5° (the infrared spectra are different), found: C, 71.61; H/D, 8.96. Refluxed with activated zinc in xylene, Ia gave 17 β -deuterioisopregnenolone acetate (III), m.p. and mixed m.p. 166–168.5°, α D -138° CHCl₃; found: C, 76.67; H/D 9.74. The n.m.r. spectrum of III shows two acetyl peaks. In the infrared spectra III lacks a band at 1170 cm.⁻¹ which appears in the spectrum of the hydrogen analog. Heated with sodium methoxide in methanol, III is isomerized with loss of deuterium to pregnenolone acetate, m.p. and mixed m.p. 140–146° (identical infrared spectra).

Hydrolysis of 17 α -hydroxypregnenolone 20-ethyl-eneketal with H₂O¹⁸ (purity 80%) afforded 20-O¹⁸-17 α -hydroxypregnenolone; λ 1655s cm.⁻¹ (C=O¹⁸), 1690w cm.⁻¹ (C=O¹⁶). Reduction with lithium aluminum hydride followed by acetylation gave Ib, m.p. 188–194°. When refluxed with activated zinc in xylene, Ib gave 20-O¹⁸-isopregnenolone acetate, m.p. 166–169°; λ 1680m cm.⁻¹ (C=O¹⁸), 1715w cm.⁻¹ (C=O¹⁶), 1740s cm.⁻¹ (acetate).

17 α -Hydroxypregnenolone was converted into the tetrahydropyranyl ether (m.p. 188–195°, found: C, 74.76; H, 9.74), which on reduction with lithium aluminum hydride gave the 20-epimeric diols: V, m.p. 186–189° (found: C, 74.42; H,

10.14), and VI, m.p. 181–182.5° (found: C, 74.21; H, 9.99). The mixture of V and VI shows a m.p. depression. The 20-monotosylate of V, m.p. 112–113° dec. (found: C, 68.31; H, 8.49) when heated with methanolic potassium hydroxide gave the oxide IV, m.p. 132.5–134° (found: C, 77.63; H, 9.86). When refluxed with activated zinc in xylene, IV afforded no isopregnenolone derivative.

Although Wagle's ionic mechanism seems to fit these results well, it probably is not fully correct since the Serini reaction proceeds also in the presence of dibenzoyl peroxide instead of activated zinc and it is inhibited completely by hydroquinone or by exclusion of atmospheric oxygen. These facts suggest that an oxygen radical participates in the Serini reaction.

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CHEMICAL INSTITUTE
FACULTY OF SCIENCE
NAGOYA UNIVERSITY
CHIKUSA, NAGOYA, JAPAN
CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

TOSHIO GOTO

LOUIS F. FIESER

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BOOK REVIEWS

Studies in Crystal Physics. Reprinted from RESEARCH, Vol. 11, 1958. By M. A. JASWON, M.A., Ph.D., Reader in Mathematics, Imperial College of Science and Technology, London. Butterworth and Co. (Canada), Ltd., 1367 Danforth Avenue, Toronto 6, Ontario, Canada. 1959. 42 pp. 18 X 24 cm. Price, \$2.25.

This refreshingly written pamphlet on several unusual aspects of Solid State Physics is based in part on the scientific papers published by the author in the last five years or so. The first four chapters are reprinted from the periodical Research; the fifth has been added to round off the story. The Chapters are: (1) Some Properties of Crystal Lattices, (2) Imperfections in Nearly Perfect Crystals, (3) X-ray Diffraction by Imperfect Crystals, (4) The Martensite Phase Change in Metals, (5) The Thermodynamic Behaviour of Solids.

The topics are treated on simplified models and with mathematics used by way of illustration rather than for derivation; wherever possible, the argument is a physical one. This makes for interesting reading, to those who are acquainted with the subject. A reader knowing nothing whatever of the topic may find himself baffled by the introduction of some terms without adequate definition, for instance on p. 9 'Edge Dislocation' (which was previously spoken of simply as 'Dislocation'), or 'Screw Dislocation' (mentioned on p. 8 but nowhere defined). Most illustrations are schematic and to the point. In Fig. 12, p. 20, back reflection rings at approximately the same angle obtained on steel with radiations of wave lengths 1.8 Å. (Co) and 0.7 Å. (Mo) can obviously not both be indexed (310) as the legend purports.

In spite of such minor defects, the author's stimulating discussion throughout, and in particular of twinning in crystals, the Austenite-Martensite transformation and the thermodynamics of first and second order transitions in metal crystals can be warmly recommended.

The book is obtainable for sh 10/6 = \$1.47 at English booksellers. Why is the Canadian publishing house permitted to surcharge this by 53%?

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P. P. EWALD

A Statistical Manual for Chemists. By EDWARD L. BAUER, Winthrop Laboratories, Rensselaer, New York. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1960. x + 156 pp. 13.5 X 21 cm. Price, \$4.75.

The author states (p. v) that, "this book was written for chemists who perform experiments, make measurements, and interpret data." It is not meant to be a complete text on statistics, but rather a manual for the working chemist. Use is made of methods of calculation (involving ranges) which require only addition, subtraction and the ability to use the slide rule.

The first chapter on fundamentals discusses experimental error, the normal distribution and "students" *t*-distribution. Examples are given to show how to compute the range, the variance and the standard deviation for small groups of data.

A chapter on the average discusses the problem of replication and shows how to compute confidence limits for an average. Data are divided into *k* small groups with *n* individuals per group. (*k* = 5; 2 < *n* < 10.) Ranges of the subgroups are computed and confidence limits set about the grand average using a table of factors corresponding to *k*, *n* and (1 - α) probability levels of 95 or 99%.

A chapter on experimental design and the analysis of variance gives a detailed explanation on how to compute and interpret the ANOVA for a two factor experiment with replication. Models and basic assumptions are listed and discussed. In the final section of this chapter the author suggests that much of the tedium of computing ANOVA