thickness before an appreciable rise in pressure is observed. For example, at a pressure of only 1 dyne per cm., the tri-*p*-cresyl thiophosphate film thickness (62.9 Å.) is over five times as great as the maximum monomolecular thickness (11.6 Å.) of tri-*p*-cresyl phosphate.

An interesting correlation between polar group structure and film properties is apparent when we consider the schematic diagrams in Fig. 1.

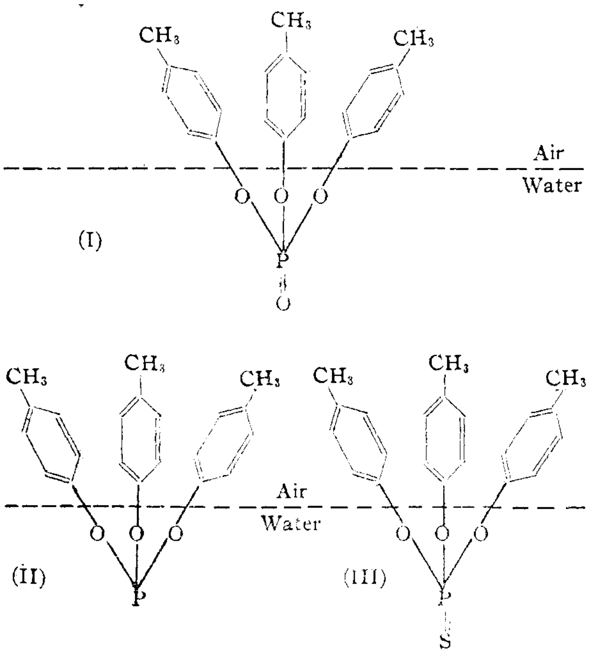

Fig. 1.—Schematic diagrams of molecular orientation at an air–water interface: (I) tri-*p*-cresyl phosphate; (II) tri-*p*-cresyl phosphite; (III) tri-*p*-cresyl thiophosphate. At expanded areas the rings are probably drawn close to the water.

The two poor film-forming compounds (II and III) differ from the tri-*p*-cresyl phosphate (I) in that they lack the P=O group. We must, therefore tentatively conclude that the important contribution to the polarity of the molecule is made by the P=O group as indicated by the superior film properties of tri-*p*-cresyl phosphate.

The most important pressure–area characteristics of a typical tri-*p*-cresyl phosphate film (27.9°) may be briefly summarized. The molecular area values at film pressures of zero (extrapolated), 5 and 8.76 dynes per cm. (the maximum) are, respectively, 99.4, 69.3 and 46.5 sq. Å. Using a density of 1.1284 g. per cc. the film thickness values at the same pressures are, respectively, 5.42, 7.78 and 11.6 Å. Partial overlapping of the molecules may perhaps account for the small areas in the final stages of the compression. The compressibility at $f = 0$, $[(a_0 - a_1)/a_0]/(f_1 - f_0)$ is 0.0607.

The above-mentioned compounds with each of the three rings attached directly to the polar group are much more compressible than the polycyclic compounds in which only one ring is attached to the principal polar group.[4] The molecular configurations of the latter type permit an approach toward vertical orientation and allow closer packing. It has been shown that films of horizontally oriented long chain molecules (polymers of ω-hydroxydecanoic acid) are much more compressible than those of vertically oriented molecules.[3] This present work indicates that perhaps the same general relationship applies to ring systems. The film compressibilities of a number of multiple ring compounds which are capable of vertical orientation range from one-sixth to about one-eighteenth that of tri-*p*-cresyl phosphate. In both types of orientation the films formed by ring compounds are, in general, more compressible than those composed of straight chain molecules. An increase in maximum film pressure with increasing vertical length of the ring system is also noted.

[4] Pressure–area relations for such a series of three-ring and five-ring compounds have been investigated and the data tabulated.[2,5]

[5] Harkins, Carman and Ries, THIS JOURNAL, **58**, 1377 (1936).

THE RESEARCH AND DEVELOPMENT DEPARTMENT
SINCLAIR REFINING COMPANY
EAST CHICAGO, INDIANA HERMAN E. RIES, JR.

RECEIVED NOVEMBER 17, 1938

THE STRUCTURE OF LUMISTEROL

Sir:

In a memoir entitled "Photochemical Interaction between Ketones and Alcohols," Weizmann, Bergmann and Hirshberg[1] in a discussion of the mechanism of ergosterol irradiation state that "at variance with the assumption of Spring[2] that this important reaction involves primarily epimerization at C_3, Windaus and Dimroth[3] were able to demonstrate that the secondary hydroxyl group at C_3 is actually not influenced by irradiation. . . ."

In the interest of accuracy it is necessary to note that in the paper cited I state that "the reactions of lumisterol, the primary photoisomeride of ergosterol, establish that it is a stereoisomer of the latter," no suggestion being made that it is the

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[1] Weizmann, Bergmann and Hirshberg, THIS JOURNAL, **60**, 1530 (1938).

[2] Spring, *Chemistry and Industry*, **55**, 837 (1936).

[3] Windaus and Dimroth, *Ber.*, **70**, 376 (1937); *cf.* Dimroth, *ibid.*, **69**, 1123 (1936).

C_3 epimer of ergosterol. In the paper (Heilbron, Moffet and Spring[4]) of which the note cited is an abstract, the conclusion reached is that ergosterol and lumisterol differ in configuration around C_{10} and that "no information is available concerning the relative orientation of the hydroxyl groups and the C_9-hydrogen atoms of the two sterols."

Again, contrary to the statement of Weizmann, Bergmann and Hirshberg, Windaus and Dimroth did not *demonstrate* that the secondary hydroxyl group is not influenced by irradiation but include in their paper the following statement: "Einen Anhaltspunkt dafür dass sterische Änderungen an der Hydroxyl-gruppe an C_3 vor sich gehen, haben wir nicht gefunden; wir halten diese Annahme für unwahrscheinlich."[5]

NOTE BY THE EDITOR.—Dr. Bergmann has written to the Editor that he regrets that the statement of Dr. Spring relative to the photo-isomerization of ergosterol was misunderstood and therefore inaccurately quoted in the article referred to.

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[4] Heilbron, Moffet and Spring, *J. Chem. Soc.*, 411 (1937).

[5] "We have found no experimental evidence that rearrangement of the hydroxyl group on C_3 occurs spontaneously, and we believe that such a change is unlikely."

THE UNIVERSITY OF MANCHESTER F. S. SPRING
MANCHESTER, ENGLAND

RECEIVED AUGUST 9, 1938

THE REDUCTION OF α-HALOGENATED KETONES: THE SYNTHESIS OF *dl*-PSEUDOEPHEDRINE

Sir:

The great advantage of aluminum isopropylate in the reduction of aldehydes and ketones lies in its specificity for the carbonyl group, side reactions such as condensation and the like being either absent or negligible. Lund [*Ber.*, **70**, 1520 (1937)] has shown this with certain ketones with primary bromine in the α-position. This reduction without removal of the α-halogen has now been tested with α-bromo ketones which have β-hydrogen available for a loss of halogen acid. The results with open chain ketones containing secondary α-bromine show that removal of bromine, and reduction to the bromohydrin, occur in about equal amounts. Thus α-bromopropiophenone with aluminum isopropylate forms the bromohydrin in about 35% yield (b. p. 73–75° (0.1 mm.)), which in turn with methylamine yields a mixture of isomeric hydroxyamines, one of which is *dl*-pseudoephedrine, m. p. 116.5–117.0°; the hydrochloride, m. p. 162–163° (over-all yield from the bromo ketone, 10%). This was identified by comparison with an authentic sample, m. p. 116.5–117.2°, mixed m. p. 116.5–117.0°, prepared from *dl*-ephedrine kindly supplied by Dr. E. H. Volwiler, Abbott Laboratories, Chicago, Illinois, and by Dr. R. H. Manske, the Canadian National Research Council, Ottawa. Contrary to expectations, no *dl*-ephedrine was found.

Cyclic secondary α-bromo ketones, and open chain tertiary α-bromo ketones, such as 2 bromocholestanone, and α-bromoisobutyrophenone, respectively, yield products almost entirely free of bromine. This work is being continued with other types of halogenated ketones.

DEPARTMENT OF CHEMISTRY PHILIP G. STEVENS
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RECEIVED NOVEMBER 21, 1938

NEW BOOKS

Tabellen und Vorschriften zur quantitativen Analyse. Gravimetrie, Elektroanalyse, Probierkunde der Edelmetalle und Gasanalyse. (Tables and Directions for Quantitative Analysis, Gravimetric, Electroanalysis, Assay of the Noble Metals, and Gas Analysis.) By W. D. TREADWELL, Professor in the United Technical Institute in Zurich. Verlagsbuchhandlung Franz Deuticke, Helferstorferstrasse 4, Wien, Germany, 1938. xii + 284 pp. 126 figs. 17.5 × 25 cm. Price, RM. 9.

The author states in the preface that his object is to present in the shortest possible form a selection of proved methods of analysis in order to make it possible for the analyst already acquainted with the fundamentals to do his work more easily. The reviewer cannot imagine any publication in which could be found more information concerning analytical chemistry contained in less than 300 pages. Here is evidence showing extreme energy on the part of the author in collecting valuable data concerning, and proved directions for determining, more than the usual list of cations and anions. It also shows his skill in collating such material in a very logical manner. About 275 references to original literature are given.

In the interest of economy of space the author has collected in one chapter the description of the common oper-