

TABLE I

| Aldehyde → Condensing agent | Acetaldehyde | | Isobutyraldehyde | | | |
|-------------------------------------|---|--|--|---|-------|-------|
| | KOH + Et ₂ NH 2,6-Dimethyl-1,3- dioxane-4-ol | Mg(Al(C ₂ H ₅) ₄) ₂ Monoacetate of 1,3- butanediol | KOH + Et ₂ NH 2,6-Diisopropyl-5,5- dimethyl-1,3-diox- ane-4-ol | Mg(Al(OC ₄ H ₉) ₄) ₂ Monoisobutyrate of 2,2,4-trimethyl- 1,3-pentanediol | | |
| Isolated product | | | | | | |
| B. p. { °C. | 68-72 | 85-89 | 90-95 | 103-105 | | |
| { Mm. | 2 | 11 | 4 | 2 | | |
| <i>n</i> ²⁵ _D | 1.4380 | 1.4190 | 1.4463 | 1.4390 | | |
| B. p. { °C. | 90-100 | 135-137 | 104-105 | 161-163 | | |
| { Mm. | 2 | 2 | 3 ^b | 1 ^a | | |
| M. p., °C. | 92-93 ^a | | 87-90 | | | |
| <i>n</i> ²⁵ _D | | 1.5045 | | 1.5575 | | |
| <i>d</i> ²⁵ | | 1.0695 | | 1.1200 | | |
| Yield, % | 47.0 | 53.2 | 33.5 | 45.0 | | |
| Benzoate Analy- ses, % | Car- bon Hydro- gen | Calcd. | 66.10 | 66.10 | 71.25 | 71.25 |
| | | Found | 66.30 | 66.26 | 67.12 | 72.01 |
| | | Calcd. | 6.78 | 6.78 | 8.75 | 8.75 |
| | | Found | 6.82 | 6.46 | 7.52 | 7.82 |

^a A slight decomposition appeared to be unavoidable. The observed molar refraction of 92.26 is in agreement with the calculated value of 92.17. ^b Distilled over as a wax-like solid. This compound was partially solidified and was extremely hygroscopic, and as a result did not give a satisfactory analysis.

with water, drying over anhydrous sodium sulfate, the ethereal solution was finally rectified.

It is obvious from the data recorded that the benzoates prepared are entirely different and that depending on the nature of the catalyst, the products of the condensation are not identical. In the case of the acetaldehyde, we were able to isolate both the dioxane and the glycol ester.

However, when the condensation of isobutyraldehyde was performed with our coordination catalyst, we obtained only the glycol ester.

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COMMUNICATIONS TO THE EDITOR

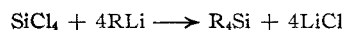
IMPROVED PROCEDURES FOR THE PREPARATION OF SOME ORGANOSILICON COMPOUNDS

Sir:

The general methods used for the synthesis of R₄Si compounds have involved reaction of silicon tetrachloride with dialkylzinc¹ compounds, with RX compounds and sodium,² and with Grignard reagents.³ The Wurtz modification was also used incidentally by Schumb and co-workers⁴ to prepare R₄Si compounds from silicon hexachloride, an RX compound and sodium. In addition, tetra-*n*-butylsilane was prepared in 50% yield from ethyl orthosilicate with a 25% excess of *n*-butylmagnesium bromide and extensive heating.⁵ These several procedures have given low to mod-

erate yields or have involved relatively drastic conditions.

Incidental to a study of the preparation of some organosilicon compounds containing functional groups, we have examined the use of organolithium compounds. We have observed that silicon tetrachloride or ethyl orthosilicate or ethyl orthothiosilicate in ether react almost immediately with the simple alkyl lithium and aryllithium compounds in ether to give excellent yields of R₄Si compounds.



With silicon tetrachloride and the appropriate RLi compound, the yield of tetraethylsilane was 92%, the yield of tetra-*n*-butylsilane was 98%, and the yield of tetraphenylsilane was 99%. From ethyl orthosilicate the yield of tetra-*n*-butylsilane was 97%, and the yield of tetraphenylsilane was 98%. The yield of tetraphenylsilane from ethyl orthothiosilicate was also 98%. Color

(1) Friedel and Crafts, *Ann.*, **127**, 28 (1863).

(2) Polis, *Ber.*, **18**, 1540 (1885).

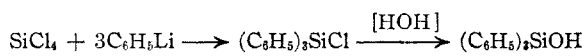
(3) Kipping, *J. Chem. Soc.*, **91**, 209 (1907); Dilthey and Eduardoff, *Ber.*, **37**, 1140 (1904).

(4) Schumb, Ackerman and Saffer, *THIS JOURNAL*, **60**, 2486 (1938).

(5) Post and Hofrichter, *J. Org. Chem.*, **5**, 572 (1940).

test I⁶ was negative immediately after the addition of the fourth equivalent of RLi compound to silicon tetrachloride or ethyl orthosilicate or ethyl orthothiosilicate.

Perhaps of greater significance is the possibility of preparing mixed organosilicon compounds conveniently and in satisfactory yields. For example, the addition of three equivalents of phenyllithium to silicon tetrachloride gave, subsequent to hydrolysis, a 97% yield of triphenylsilanol.



And the addition of three equivalents of phenyllithium to silicon tetrachloride, followed by the addition of one equivalent of *p*-tolyllithium, gave a 91% yield of triphenyl-*p*-tolylsilane; m. p., 134–135° (from ethyl acetate-methanol).

Anal. Calcd. for C₂₅H₂₂Si: Si, 8.00. Found: Si, 7.92.

The yield of diphenyl-di-*p*-tolylsilane by the addition of two equivalents of phenyllithium (or *p*-tolyllithium) followed by two equivalents of *p*-tolyllithium (or phenyllithium) was 78%; m. p., 176–177° (from ethyl acetate-methanol).

Anal. Calcd. for C₂₆H₂₄Si: Si, 7.70. Found: Si, 7.60.

(6) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925). With some sterically hindered radicals in the RLi compounds, the fourth R group is introduced more slowly.

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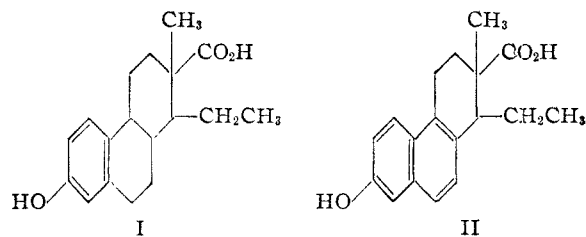
HENRY GILMAN
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RECEIVED JULY 15, 1946

1-ETHYL-2-METHYL-7-HYDROXY-1,2,3,4,9,10,11,12-OCTAHYDROPHENANTHRYL-2-CARBOXYLIC ACID

Sir:

In 1944 Miescher¹ described, in a general fashion, the isolation of an active estrogen, "Doisynsäure" (I), from the alkali degradation of estradiol.



In the same article,¹ the author indicated the isolation of a more active substance, "Bisdehydrodoisynsäure" (II) from an analogous degradation of equilenin and dihydroequilenin.

More recently Miescher and co-workers² have given detailed descriptions of these degradations, the synthesis of the tetrahydro acid II, as well as

(1) Miescher, *Helv. Chim. Acta*, **27**, 1727 (1944).

(2) Miescher, *et al.*, *ibid.*, **28**, 156, 991, 1342, 1506 (1945); **29**, 586 (1946).

several of its 1- and 2-alkyl derivatives and certain related compounds.

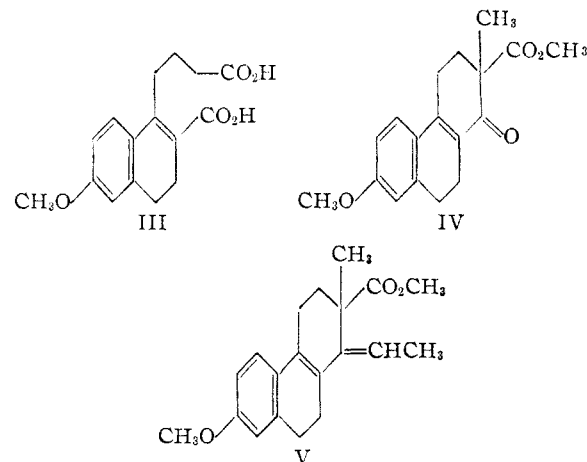
The total synthesis of the octahydro acid I has now been effected in This Laboratory, and the resulting mixture of diastereoisomers has been found to exhibit an order of estrogenic activity essentially identical with the estradiol degradation product (I).¹

Esterification of *m*-methoxyphenylacetic acid³ and reduction of the ester with sodium and alcohol gave β -*m*-methoxyphenylethyl alcohol which, with phosphorus tribromide, yielded the corresponding phenylethyl bromide. Condensation of the latter with ethyl β -ketopimelate,⁴ followed by cyclodehydration with concentrated sulfuric acid and subsequent alkaline hydrolysis, gave the dibasic acid (III)⁵ which was converted into the unsaturated keto ester (IV) by the method of Bachmann, Kushner and Stevenson.⁶ Treatment of IV with a titrated equivalent of ethylmagnesium iodide yielded the ethylidene derivative (V); m. p. 144–145°.

Anal. Calcd. for C₂₀H₂₄O₃: C, 76.8; H, 8.15. Found: C, 76.4; H, 8.22.

Catalytic reduction of the diene (V) followed by hydrolysis and demethylation of the crude hydrogenation product gave I (diastereoisomeric mixture) as a white, amorphous solid melting unsharply at 90–110°.

Anal. Calcd. for C₁₈H₂₄O₃· $\frac{1}{2}$ H₂O: C, 72.8; H, 8.48. Found: C, 72.1; H, 8.01.



When bio-assayed by the Kahnt-Doisy method, using pure estrone as a standard, the product gave the typical estrus response in doses of 0.8 to 0.9 gamma.

Conversion of the above hemihydrate into the benzylammonium salt and subsequent decomposition with dilute mineral acid yielded the anhydrous compound melting at about 95°.

(3) Schwenk and Bloch, *THIS JOURNAL*, **64**, 3051 (1942).

(4) Prepared according to the β -ketoester synthesis of Breslow, Baumgarten and Hauser, *ibid.*, **66**, 1286 (1944).

(5) Bachmann, Kushner and Stevenson, *ibid.*, **64**, 977 (1942).

(6) Reference 5, p. 978.

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 75.0; H, 8.39.
Found: C, 75.1; H, 8.29.

Hydrolysis and demethylation of V gave an unsaturated phenolic acid (VI), m. p. 217–219, which produced the full estrus response at levels of 0.33 gamma.

A detailed description of this work will be reported later.

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NEW BOOKS

Rocks and Rivers. By ELLIS W. SHULER, Southern Methodist University, Dallas, Texas. The Jaques Cattell Press, Lancaster, Pennsylvania, 1945. xx + 300 pp. 16 × 24 cm. Price, \$4.00.

Time was, a century or more ago, when a scientist might aspire to a fair acquaintance with all of what was then called Natural Science, but now in this Atom Age a chemist's own special field usually is too large for him to master. However, nearly every chemist has a side interest elsewhere in the field of science; for some years the reviewer has enjoyed reading, studying, working and looking at geology and geography; hence this new book by Dr. Shuler has for him an eloquent and fascinating message.

In the Preface the author says: "... Geologists, as most scientists, have been afraid to show any feeling for the larger scope, the cultural interest, the wonder of their science. . . . so that the whole modern science of geology is now entombed in highly technical fact-telling records. . . . An attempt is made to glorify the common phenomena rather than the odd or unusual. . . . The method of presentation is by story and illustration. . . . The topics selected are those of everyday observation. . . ." and the author has succeeded very well in his task "... of making the landscape understandable to every traveler" and observer, both by words and a fine selection of less-often-seen illustrations.

The 300-odd pages of the book are divided among sixteen chapters, which in simple words carry the reader all over the earth's surface, but principally in the United States, and introduce him to crystals, gems, dirt, sedimentary rocks, the earth's surface, earth movements, landscape changes, weathering effects of wind, frost, water both running and ocean, landslides, erosion, glaciation, windblown earth, soil and its formation, loss and conservation methods, rock and its sculpturing, mesas and bad lands, small and large springs, water table, plain and artesian wells, hot springs and geysers, underground waters and their work, caves, sinkholes, natural bridges, the ocean as an engineer, beaches and their activity, volcanic activity, both modern and ancient and the building of mountains, the ice age theory and its evidence, glaciation and its remains, rivers, their work and ceaseless attack on mountains, Major Powell, lakes both past and present (Lake Bonneville), Niagara River and Falls, the Arkansas River and its Royal Gorge, the Colorado, the Merced, the Yellowstone, the Snake and Columbia, individual mountains and their history, useful ores and minerals with their locations and availability, and the age of the earth. This is an imposing list of topics, subjects and objects which any traveler may see and not appreciate; "Rocks and Rivers" is an illustrated lecture to assist him in seeing, believing and understanding.

ALLEN D. BLISS

Physical Chemistry of Cells and Tissues. By RUDOLF HÖBER, University of Pennsylvania School of Medicine, Philadelphia, Pa. With the Collaboration of David I. Hitchcock, J. B. Bateman, David R. Goddard and Wallace O. Fenn. The Blakiston Company, 1012 Walnut Street, Philadelphia 5, Pa. (Toronto), 1945. xiii + 676 pp. 70 illustrations. 16 × 24 cm. Price, \$9.00.

This is a book of remarkable interest and value in many respects. Its character may be indicated by a brief discussion of the eight sections into which it is divided.

Section I, by Hitchcock, presents some selected principles of physical chemistry, including diffusion in liquids, reaction velocity and enzyme action, the elements of thermodynamics, electromotive force measurements and some of the osmotic and electrical properties of aqueous solutions. The treatment is definitely not on an elementary level; some knowledge of the calculus, and some previous acquaintance with the fundamentals of physical chemistry, are assumed. For students so equipped, the discussion given here should be of great value. Many relevant subjects were, of necessity, omitted; one may regret that the treatment of oxidation-reduction potentials is so brief.

Section II, by Bateman, deals with interatomic and intermolecular forces, and with the properties of large molecules in solution, in the solid state and in the form of films and membranes. To a reader with some previous background in this field, the discussion may be recommended as most illuminating and suggestive throughout. Those without some previous knowledge in this area may find the treatment highly condensed in places. There are frequent allusions to matters which the reader is expected to know and which may not always be well known, even to many with a good knowledge of general physical chemistry. In the discussion of dielectric measurements, for instance, it would have been useful to give a more explicit discussion of the relation between the dielectric constant and the dipole moment, in polar liquids and solutions; and some additional figures and diagrams would have been helpful. Nevertheless, this is a remarkably interesting and thoughtful discussion of the field it covers.

The following three sections—Introductory Remarks Concerning the Architecture of Protoplasm; The Surface of the Protoplast, Its Properties and Its Architecture; Influence of Some Extracellular Factors on Cellular Activity—are written by Dr. Höber himself. In the general character of their subject matter they follow closely the pattern of the author's earlier "Physikalische Chemie der Zelle und der Gewebe." The entire discussion, however, has been rewritten throughout, and takes account of all the more recent developments in this area. From the point of view of the physical chemist, the systems discussed are extremely complex; although from the point of view of the biologist, they may be relatively simple. The answers suggested are necessarily tentative, with frequent gaps and