TABLE I

Aldehyde →			Acetaldehyde		Isobutyraldehyde	
Condensing agent			KOH + Et_2NH	$Mg(Al(C_2H_5)_4)_2$	KOH + Et_2NH	$Mg(Al(OC_4H_9)_4)_2$
Isolated product			2,6-Dimethyl-1,3-dioxane-4-ol	Monoacetate of 1,3-butanediol	2,6-Diisopropyl-5,5-dimethyl-1,3-dioxane-4-ol	Monoisobutyrate of 2,2,4-trimethyl-1,3-pentanediol
B. p.	°C.		68–72	85–89	90–95	103–105
	Mm.		2	11	4	2
$n^{25}D$			1.4380	1.4190	1.4463	1.4390
Benzoate: B. p.	°C.		90–100	135–137	104–105	161–163
	Mm.		2	2	3[b]	1[a]
M. p., °C.			92–93[3]	....	87–90	....
$n^{25}D$			....	1.5045	....	1.5575
d^{25}			....	1.0695	....	1.1200
Yield, %			47.0	53.2	33.5	45.0
Analyses, %	Carbon	Calcd.	66.10	66.10	71.25	71.25
		Found	66.30	66.26	67.12	72.01
	Hydrogen	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 coördination catalyst, we obtained only the glycol ester.

COMMUNICATION NO. 46 FROM
THE DEPARTMENT OF ORGANIC CHEMISTRY
FORDHAM UNIVERSITY, NEW YORK 58, N. Y.

RECEIVED DECEMBER 29, 1945

COMMUNICATIONS TO THE EDITOR

IMPROVED PROCEDURES FOR THE PREPARATION OF SOME ORGANOSILICON COMPOUNDS

Sir:

The general methods used for the synthesis of R_4Si compounds have involved reaction of silicon tetrachloride with dialkylzinc[1] compounds, with RX compounds and sodium,[2] and with Grignard reagents.[3] The Wurtz modification was also used incidentally by Schumb and co-workers[4] to prepare R_4Si 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 moderate 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 alkyllithium and aryllithium compounds in ether to give excellent yields of R_4Si compounds.

$$SiCl_4 + 4RLi \longrightarrow R_4Si + 4LiCl$$

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

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(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 I[6] 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.

$$SiCl_4 + 3C_6H_5Li \longrightarrow (C_6H_5)_3SiCl \xrightarrow{[HOH]} (C_6H_5)_3SiOH$$

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 $C_{25}H_{22}Si$: 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 $C_{26}H_{24}Si$: Si, 7.70. Found: Si, 7.60.

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[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.

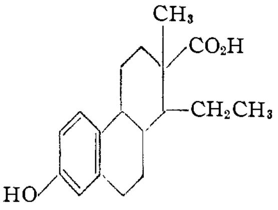
CHEMICAL LABORATORY
IOWA STATE COLLEGE HENRY GILMAN
AMES, IOWA RUSSELL N. CLARK

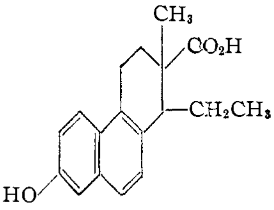
RECEIVED JULY 15, 1946

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

Sir:

In 1944 Miescher[1] described, in a general fashion, the isolation of an active estrogen, "Doisynolsäure" (I), from the alkali degradation of estradiol.


I


II

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

More recently Miescher and co-workers[2] have given detailed descriptions of these degradations, the synthesis of the tetrahydro acid II, as well as several of its 1- and 2-alkyl derivatives and certain related compounds.

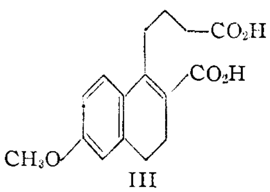
The total synthesis of the octahydro acid I has now been effected in This Laboratory, and the resulting mixture of diastereoisomers has been found to exhibit an order of estrogenic activity essentially identical with the estradiol degradation product (I).[1]

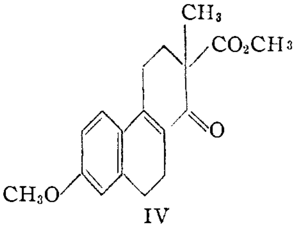
Esterification of *m*-methoxyphenylacetic acid[3] and reduction of the ester with sodium and alcohol gave β-*m*-methoxyphenylethyl alcohol which, with phosphorus tribromide, yielded the corresponding phenylethyl bromide. Condensation of the latter with ethyl β-ketopimelate,[4] followed by cyclodehydration 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 ethylidine derivative (V); m. p. 144–145°.

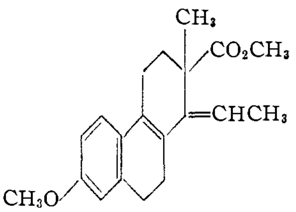
Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.8; H, 8.15. Found: C, 76.4; H, 8.22.

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 $C_{18}H_{24}O_3 \cdot {}^1/_2H_2O$: C, 72.8; H, 8.48. Found: C, 72.1; H, 8.01.


III


IV


V

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°.

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

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

[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.