and alcohols has been reported to be catalyzed by boron trifluoride-etherate.[2] We have found this reagent also to be effective in catalyzing the methylation of alcohols with diazomethane.[3] For example, the yield of β-cholestanol methyl ether was essentially unchanged by replacing the fluoroboric acid catalyst with an equimolar amount of boron trifluoride etherate.

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[2] M. S. Newman and P. F. Beal, THIS JOURNAL, **72**, 5161 (1950).

[3] Since this manuscript was written, similar observations were reported by E. Müller and W. Rundel, *Angew. Chem.*, **70**, 105 (1958).

CONTRIBUTION NO. 2332
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RECEIVED APRIL 14, 1958

CONDENSATION OF TRIMETHYLSILANOL WITH TITANIUM ISOPROPYLATE

Sir:

The preparation of glassy polymeric products containing Si–O–Ti bonds has been reported.[1] Because of interest in modified polymers, it seems worthwhile to report a simple synthesis of several monomeric compounds containing silicon and titanium.

The synthesis involves mixing trimethylsilanol and titanium isopropylate in the molar ratios desired in the product, usually in a solvent, and distilling to recover substantial yields of the product.

A typical preparation for $Ti[OSi(CH_3)_3]_4$ is given. To 0.1 mole (28.4 g.) freshly distilled titanium isopropylate in a 125-ml. distilling flask was added 70 ml. of 5.77 molar trimethylsilanol (0.4 mole) in dibutyl ether. The mixture became warm, was allowed to stand for about an hour, then distilled in vacuum to remove ether solvent and recover the reaction product. With no special precautions the recovery was 50–70% of theoretical.

The products obtained in separate preparations using appropriate ratios of silanol to titanium isopropylate are summarized in Table I.

TABLE I

Formula		$Ti(OC_3H_7)_3$-$(OSi(CH_3)_3)$	$Ti(OC_3H_7)_2$-$(OSi(CH_3)_3)_2$	$Ti(OSi$-$(CH_3)_3)_4$
Carbon, %	Calcd.	45.85	41.83	35.65
	Found	45.71	41.65	35.81
Hydrogen, %	Calcd.	9.62	9.36	8.98
	Found	9.48	9.33	9.05
$n^{22}D$		1.4490	1.4408	1.4300
B.p.	°C.	114	120	100
	Mm.	13	14	2

The condensation product containing two silanols and two isopropyl groups would be expected to exhibit two arrangements if the titanium is square and planar. No separation was attempted.

Each of the titanium products was a water white liquid as prepared, but those containing isopropoxy groups developed an intense blue on standing for several months in sealed capsules.

Volatile products incompletely characterized were obtained by the distillation of trimethylsilanol and aluminum isopropylate.

The use of diethylsilanediol in place of trimethylsilanol with the appropriate isopropylate gave non-volatile polymeric substances which have not been characterized.

Acknowledgment.—This work has been supported by the Office of Naval Research.

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[1] K. A. Andrianov, T. N. Janina and E. N. Khrustaleva, *Izvest. Akad. Nauk, S.S.S.R.*, *otdel, Khim. Nauk*, 798–804 (1956); *Chem. Abstr.*, **51**, 3487 (1957).

DEPARTMENT OF CHEMISTRY
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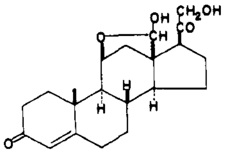
RECEIVED FEBRUARY 15, 1958

TOTAL SYNTHESIS OF ALDOSTERONE

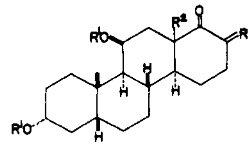
Sir:

We disclose herewith a preparation of the adrenal hormone aldosterone (I) by a highly stereoselective total synthesis which is basically different from previous approaches.[1]

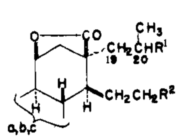
The dihydroxy-ketone II(R^1 = H, R^2 = βH, R^3 = H_2)[2] was converted into the 17-furfurylidene derivative (R^3 = CHC_4H_3O) m.p. 193–194° which, on treatment with methacrylonitrile in methanolic methoxide, was transformed into the adduct II (R^1 = H, R^2 = $-CH_2CH(CH_3)CN$, R^3 = CHC_4H_3O).[3,4] Acetylation, followed by ozonolysis, then



I



II



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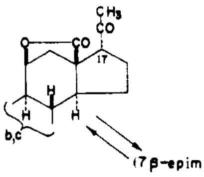
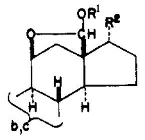
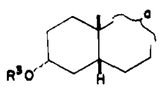


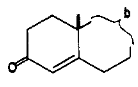
IV

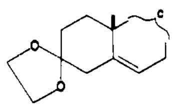
V



VI







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[1] (a) J. Schmidlin, G. Anner, J. R. Billeter and A. Wettstein, *Experientia*, **11**, 365 (1955), *et seq.* to J. S. Schmidlin, G. Anner, J. R. Billeter, K. Heusler, H. Ueberwasser, P. Wieland and A. Wettstein, *Helv. Chim. Acta*, **40**, 2291 (1957); (b) A. Lardon, O. Schindler and T. Reichstein, *ibid.*, **40**, 666 (1957).

[2] W. S. Johnson, R. Pappo and W. F. Johns, THIS JOURNAL, **78**, 6339 (1956).

[3] This product was a mixture of C_{20} epimers that could be employed in the succeeding steps without separation because the asymmetry of C_{20} was ultimately eliminated. In the preliminary study the mixture was separated at the diketone stage 111a (R^1 = R^2 = $COCH_3$, R^3 = Ac) and each epimer examined separately in the succeeding reactions.

[4] *Cf.* W. S. Johnson, D. G. Martin, R. Pappo, S. D. Darling and R. A. Clement, *Proceedings*, 58 (1957).

saponification, gave on acidification the lactone-dicarboxylic acid IIIa ($R^1 = R^2 = CO_2H$, $R^3 = H$)[3] which was transformed, through reaction of the diacid chloride acetate IIIa ($R^1 = R^2 = COCl$, $R^3 = Ac$) with dimethylketene acetal,[5] into the diketo-lactone IIIa ($R^1 = R^2 = COCH_3$, $R^3 = Ac$) [isomer a, m.p. 172–173°; isomer b, m.p. 145–146°].[3] Rearrangement with trifluoroperacetic acid[6] afforded the triacetate IIIa ($R^1 = R^2 = OAc$, $R^3 = Ac$) [isomer a, m.p. 140–141°; isomer b, m.p. 142–143°][3] which, on mild saponification followed by N-bromoacetamide oxidation and reacetylation, gave the 3-ketodiacetate [isomer a, m.p. 135–136°; isomer b, m.p. 147–148.5°].[3] Bromination and dehydrobromination[7] afforded the unsaturated ketone IIIb ($R^1 = R^2 = OAc$) [isomer a, m.p. 183–184°; isomer b, m.p. 154–155°],[3] which was converted[8] into the ketal IIIc ($R^1 = R^2 = OAc$) [isomer a, m.p. 155–156°; isomer b, m.p. 175–176°].[3] Saponification gave the diol IIIc ($R^1 = R^2 = OH$), [isomer a, m.p. 185–186°; isomer b, m.p. 205–207°] which was transformed, by selective reaction with 2,5-dimethylbenzenesulfonyl chloride in pyridine, into the monoester IIIc ($R^1 = OH$, $R^2 = OSO_2C_6H_3Me_2$). Oxidation with Sarett's reagent converted the C_{20} hydroxyl to ketone; thus both epimers yielded the same product[3] which, with potassium *t*-butoxide, underwent cyclization[9] to the keto-lactone IVc, m.p. 194–196°. This substance was partially isomerized by base into the 17β epimer Vc, m.p. 210–214° (reported,[1a] 202–208°). The latter substance and the corresponding ketone Vb, m.p. 215–219° (reported,[1a] 218–220°) were shown, by infrared and mixed m.p. comparisons, to be identical with authentic specimens.[10] Vc has been converted into aldosterone.[1a]

Although our main objective was thus realized we hoped to obviate certain difficulties attending the last stages of the synthesis due to the β-oriented C_{17} side-chain[1a] by operating in the 17α series. With two mole-equivalents of lithium aluminum hydride IVc was selectively reduced to the lactol VIc ($R^1 = H$, $R^2 = CHOHCH_3$), m.p. 190–194°, which was hydrolyzed to VIb ($R^1 = H$, $R^2 = CHOHCH_3$), m.p. 127–133°, then treated with methanol and acid to yield the lactol ether VIb ($R^1 = CH_3$, $R^2 = CHOHCH_3$), m.p. 168–169.5°. Oxidation with Sarett's reagent afforded the ketone VIb ($R^1 = CH_3$, $R^2 = COCH_3$), m.p. 166–168°, which was converted[11] into the 21-acetoxy compound VIb ($R^1 = CH_3$, $R^2 = COCH_2OAc$), m.p. 138–140°. Hydrolysis of the lactol ether with 70% acetic acid gave *dl*-17α-aldosterone-21-acetate, VIb ($R^1 = H$, $R^2 = COCH_2OAc$), m.p. 166–170°. The infrared spectrum was identical with that[10] of material obtained by partial isomerization of the 17β-epimer.[1a] Treatment of VIb ($R^1 = H$, $R^2 = COCH_2OAc$) with potassium carbonate in aqueous methanol gave the C_{17} epimeric mixture [1a] from which *dl*-aldosterone readily was isolated. The product was identified with authentic material[10] by paper chromatographic behavior, infrared spectroscopy and physiological activity.[12,13]

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(5) S. M. McElvain and G. R. McKay, Jr., THIS JOURNAL, **78**, 6086 (1956).

(6) *Cf.* W. D. Emmons and G. B. Lucas, *ibid.*, **77**, 2287 (1955).

(7) *Cf.* R. P. Holysz, *ibid.*, **75**, 4432 (1953).

(8) *Cf.* H. J. Dauben, B. Löken and H. J. Ringold, *ibid.*, **76**, 1359 (1954).

(9) *Cf.* W. F. Johns, R. M. Lukes and L. H. Sarett, *ibid.*, **76**, 5026 (1954).

(10) Kindly supplied by Dr. Wettstein.

(11) J. A. Hogg, P. F. Beal, A. H. Nathan, F. H. Lincoln, W. P. Schneider, B. J. Magerlein, A. R. Hanz and W. R. Jackson, THIS JOURNAL, **77**, 4438 (1955).

(12) Satisfactory analytical data have been obtained for the new substances reported above.

(13) We are grateful to the Sterling-Winthrop Research Institute, the Upjohn Company, the Wisconsin Alumni Research Foundation and the National Science Foundation for assistance.

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RECEIVED APRIL 18, 1958

THE COMPLEX FORMED FROM COBALT HYDROCARBONYL AND BUTADIENE

Sir:

Although Prichard has reported the preparation of a complex between butadiene and dicobalt octacarbonyl under Oxo conditions,[1] only an analysis for cobalt and an analysis by the Orsat technique of the sulfuric acid decomposition products were given.

We have now been able to prepare and study the stereochemical configuration of the complex formed between butadiene and cobalt hydrocarbonyl in the absence of Oxo conditions.

Potassium cobaltcarbonylate was made to react with glacial acetic acid and liquid butadiene in a high pressure vessel. After twelve hours, a red-brown liquid, distilling at 33–35° at less than 1 mm. pressure, was obtained.

Analysis showed it to have the empirical composition $Co(CO)_3C_4H_7$. In benzene it gave a molecular weight of 195, compared to a calculated molecular weight of 198. The compound is diamagnetic and contains no acidic hydrogen.

The infrared and ultraviolet absorption characteristics indicate the disappearance of the conjugated diolefin structure and the appearance of a structure producing absorption characteristics similar to those of *cis* monoölefins. The sharp peak at 703 cm.$^{-1}$ which in the cobalt hydrocarbonyl has been assigned[2,3] to the hydrogen vibrations also has disappeared.

However, carbon monoxide could react with butadiene to give cyclopentanone, which might have some aromatic character and give a complex similar to cyclopentadiene bis-carbonyl cobalt; however, the infrared data do not seem to be in line with such a structure.

Experimental details and a reinterpretation of the mechanism of the oxo reaction[4,5,6] will be reported shortly.

Thanks are due to Drs. L. Orgel and H. W. Stern-

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(1) William W. Prichard, U. S. Patent 2,600,571 (June 17, 1952).

(2) W. F. Edgell, Ch. Magee, and G. Gallup, THIS JOURNAL, **78**, 4185 (1956).

(3) J. W. Cable and R. K. Sheline, *Chem. Rev.*, **56**, 1 (1956).

(4) A. R. Martin, *Chem. and Ind.*, 1936 (1954).

(5) G. Natta, R. Ercoli, G. Castellano and P. H. Barbieri, THIS JOURNAL, **76**, 4049 (1954).

(6) I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *ibid.*, **78**, 5401 (1956).