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).

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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).

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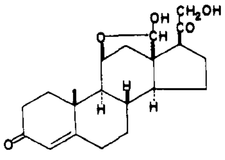
RECEIVED FEBRUARY 15, 1958

TOTAL SYNTHESIS OF ALDOSTERONE

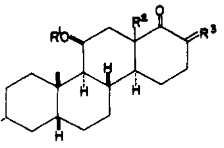
Sir:

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]

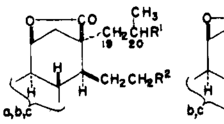
The dihydroxy-ketone II(R^1 = H, R^2 = βH, R^3 = H_2)[2] was converted into the 17-furfurylidene derivative (R^3 = CHC_4H_3O) m.p. 193–194° which, on treatment with methacrylonitrile in methanolic methoxide, was transformed into the adduct II (R^1 = H, R^2 = $-CH_2CH(CH_3)CN$, R^3 = CHC_4H_3O).[3,4]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

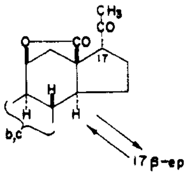


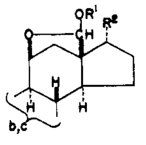
I



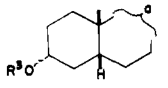
II

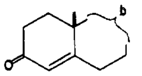


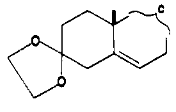




III IV V VI







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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 IIIa (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).