solved in water and heated with sodium carbonate. The liberated base was extracted with ether. The ethereal solution was washed thoroughly with water until neutral and evaporated. The base was converted into the D-glutamic acid salt and purified as described above. The purified base gave a triacetyl derivative melting at 98–100° ($[\alpha]^{22}D$ +19.2 (0.1 g. in 10 cc. of chloroform)).

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THE PREPARATION OF D-HOMOPROGESTERONE AND D-HOMO-11-DEOXYCORTICOSTERONE ACETATE

Sir:

The sustained interest in the cortical hormones made it desirable to determine the effect of a six-membered D ring on cortical-hormonal activity. D-Homoprogesterone and D-homo-11-deoxycorticosterone acetate were prepared as the first part of this program.

Ethynylation of 3β-hydroxy-D-homoandrost-5-en-17a-one[1] (I) produced D-homo-17aα-pregn-5-en-20-yne-3β,17aβ-diol (II), m.p. 262–264°; $[\alpha]^{23}D$ −108° (0.5% in $CHCl_3$); (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.2; H, 9.8); and, in low yield, D-homopregn-5-en-20-yne-3β,17aα-diol (III), m.p. 220–222°; $[\alpha]^{23}D$ −76° (1% in $CHCl_3$); (*Anal.* Found: C, 80.2; H, 10.0.) Treatment of either II or III with formic acid[2] gave, after hydrolysis, 3β-hydroxy-D-homopregna-5,17(17a)-dien-20-one (IV), m.p. 233–235°; $[\alpha]^{23}D$ +35° (0.5% in $CHCl_3$); $\lambda_{max.}$ 233 mμ, ε 8,930; (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.7; H, 9.9.) plus an unidentified compound, $C_{22}H_{30}O$, m.p. 171–172°. Hydrogenation of IV yielded 3β-hydroxy-D-homopregn-5-en-20-one (V), m.p. 205–206°, $[\alpha]^{23}D$ −25° (1% in $CHCl_3$); (*Anal.* Calcd. for $C_{22}H_{34}O_2$: C, 80.0; H, 10.4. Found: C, 79.8; H, 10.3) which on Oppenauer oxidation gave the desired D-homoprogesterone, m.p. 158–160°; $[\alpha]^{23}D$ +167° (1% in $CHCl_3$); $\lambda_{max.}$ 242 mμ, ε 16,600; (*Anal.* Calcd. for $C_{22}H_{32}O_2$: C, 80.4; H, 9.8. Found: C, 80.5; H, 9.6.) Since attempts to isomerize D-homoprogesterone, by heating in acidic and in basic solution, failed, the configuration of the side chain at 17a is probably β.

Perfusion of D-homoprogesterone through surviving adrenal glands yielded neither D-homocorticosterone nor 17aα-hydroxy-D-homocorticosterone.

D-Homo-11-deoxycorticosterone acetate was prepared from V by use of the method devised by H. Ruschig.[3] Compound V was condensed with dimethyl oxalate using sodium methoxide in benzene. The sodium enolate so obtained was iodinated in methanol at −15°, then cleaved to 3β-hydroxy-21-iodo-D-homopregn-5-en-20-one (VI) with sodium methoxide at room temperature. The crude iodo compound (VI) was converted, by means of potassium acetate in acetone, to 3β,21-dihydroxy-D-homopregn-5-en-20-one 21-acetate (VII), m.p. 188–190°; (*Anal.* Calcd. for $C_{24}H_{36}O_4$: C, 74.2; H, 9.3. Found: C, 74.3; H, 9.6.) Oppenauer oxidation of VII yielded D-homo-11-deoxycorticosterone acetate (VIII), m.p. 152–154°; $[\alpha]^{23}D$ +150° (0.45% in $CHCl_3$); $\lambda_{max.}$ 241 mμ, ε 16,200; (*Anal.* Calcd. for $C_{24}H_{34}O_4$: C, 74.6; H, 8.9. Found: C, 74.9; H, 8.9). Compound VIII showed no appreciable ability to prevent sodium excretion in adrenalectomized rats,[4] but it did possess approximately 10% of the activity of 11-deoxycorticosterone acetate in the maintenance of life in adrenalectomized rats on a sodium deficient diet.[5]

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MAGNETIC CATALYSIS OF A DECARBOXYLATION REACTION[1]

Sir:

There is now a considerable body of experimental evidence[2] that the rate of decarboxylation of C^{13} substituted carboxylic acids is appreciably higher that would be expected from the rate of decarboxylation of the C^{12}- and C^{14}-compounds on the basis of change of isotopic mass alone.

A possible cause of this apparent anomaly could lie in the nonzero nuclear spin and magnetic moment of C^{13}. Both C^{12} and C^{14} have zero values for these properties. A paramagnetic rare earth ion such as dysprosium at a distance of a few angströms from the C–C bond could cause an inhomogeneous magnetic field comparable to that caused by a C^{13} nucleus at one end of the bond.

We have now found such an acceleration of the rate of decarboxylation of (natural) phenylmalonic acid in aqueous solution at 45° in the presence of 0.5 *N* dysprosium ion.

The kinetics of the decarboxylation of phenylmalonic acid have been explored.[3] The conditions selected for the present experiments, *p*H 0.4–0.8, yield a first order reaction of un-ionized phenylmalonic acid to phenylacetic acid with a rate almost independent of *p*H. Experiments were carried out with phenylmalonic acid alone and in the presence of 0.5 *N* La^{3+}, Y^{3+} and Dy^{3+} as rare earth chlorides. The initial *p*H of the reaction mixtures was equalized by addition of standard hydrochloric acid. A dozen aliquots were withdrawn at intervals during the first 50% of reaction,

(1) This work was assisted by the American Petroleum Institute through Research Project 50. The dysprosium was kindly made available to us by Dr. F. H. Spedding.

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